

Editor
ROY WALDO MINER

BRANCHED MOLECULES

BY

F. R. EIRICH (*Conference Chairman*), C. O. BECKMANN, J. D. COTMAN, JR.,
M. FIXMAN, P. J. FLORY, T. G. FOX, S. GRATCH, H. MARK, P. A. MARSHALL,
M. MORTON, S. ROTHMAN, F. M. RUGG, J. J. SMITH, W. H. STOCKMAYER, M.
WALES, L. H. WARTMAN, S. G. WEISSBERG, O. L. WHEELER, AND B. H. ZIMM

Consulting Editor
FREDERICK R. EIRICH



NEW YORK
PUBLISHED BY THE ACADEMY

November 19, 1953

THE NEW YORK ACADEMY OF SCIENCES
(Founded in 1817)

COUNCIL, 1953

President

DAVID B. STEINMAN

President-Elect

PAUL FEJOS

Vice-Presidents

ELMORE H. NORTHEY

MAURICE L. TANTER

Recording Secretary

JOHN TEE-VAN

Corresponding Secretary

JUNIUS BIRD

Treasurer

DONALD M. BENJAMIN

Editor

ROY WALDO MINER

Elected Councilors

1951-1953

EDWIN J. DE BEER

OSKAR P. WINTERSTEINER

ROSS F. NIGRELLI

1952-1954

WILLIAM H. COLE

CHARLES H. TOWNES

CLIFFORD J. RASSWEILER

1953-1955

EDWARD J. KEMPF
BORIS PREGEL

ROBERT P. PARKER
JOHN TURKEVICH

Finance Committee

ROBERT F. LIGHT, *Chairman*

GORDON Y. BILLARD

HARDEN F. TAYLOR

Executive Director

EUNICE THOMAS MINER

SECTION OF GEOLOGY AND MINERALOGY

THOMAS N. WALTHIER, *Chairman*

ANGELINA ROSE MESSINA, *Secretary*

SECTION OF BIOLOGY

M. J. KOPAC, *Chairman*

HILARY KOPROWSKI, *Secretary*

DIVISION OF MYCOLOGY

SAMUEL M. PECK, *Chairman*

LINDSAY S. OLIVE, *Secretary*

SECTION OF PSYCHOLOGY

NEWMAN L. HOOPINGARNER, *Chairman*

ALBERTA S. GILINSKY, *Secretary*

SECTION OF ANTHROPOLOGY

WILLIAM L. THOMAS, JR., *Chairman*

JOHN L. LANDGRAF, *Secretary*

SECTION OF PHYSICS AND CHEMISTRY

FRANK BRESCIA, *Chairman*

CECIL V. KING, *Secretary*

SECTION OF OCEANOGRAPHY AND METEOROLOGY

PETER E. KRAGHT, *Chairman*

WALTER BOEHNER, *Secretary*

SECTION OF MATHEMATICS AND ENGINEERING

SEBASTIAN B. LITTAUER, *Chairman*

DAVID B. HERTZ, *Secretary*

These Sections and the Division hold meetings regularly, one evening each month, during the academic year, October to May, inclusive.

Two-day conferences also are held at irregular intervals. All meetings are held at the building of The New York Academy of Sciences, 2 East Sixty-third Street, New York 21, New York.

ANNALS OF THE NEW YORK ACADEMY OF SCIENCES

VOLUME 57, ART. 4, PAGES 325-450

November 19, 1953

Editor

ROY WALDO MINER

BRANCHED MOLECULES*

RECEIVED

DEC 3 1953

H. W. H.

Consulting Editor

FREDERICK R. EIRICH

CONTENTS

Introduction to Branched Molecules. By P. J. FLORY	327
Physical Properties of Solutions of Branched Polymers. By BRUNO H. ZIMM	332
Dilute Solutions of Branched Polymers. By WALTER H. STOCKMAYER AND MARSHALL FIXMAN	334
Application of Viscosity Methods to the Study of Branching in Polysaccharides. By M. WALES, P. A. MARSHALL, S. ROTHMAN, AND S. G. WEISSBERG	353
Relation Between Degree of Branching and Degree of Conversion During Polymerization. By O. L. WHEELER	360
Crosslinking in Monovinyl Monomers. (I). By Chain Transfer with the Polymer Chain. By T. G. FOX AND SERGE GRATCH	367
The Structure of Amylopectin and Glycogen. By CHARLES O. BECKMANN	384
Branching in Polyethylene. By FRANK M. RUGG, JOSEPH J. SMITH, AND LLOYD H. WARTMAN	398
Studies on Polyvinyl Chloride. (II). Branching. By JOHN D. COTMAN, JR.	417
Branching in Dienes. By MAURICE MORTON	432
Branching by Long Chain Substituents. By H. MARK	445

* This series of papers is the result of a Conference on Branched Molecules, held by the Section of Physics and Chemistry of The New York Academy of Sciences, January 9 and 10, 1953.

Copyright, 1953, by The New York Academy of Sciences

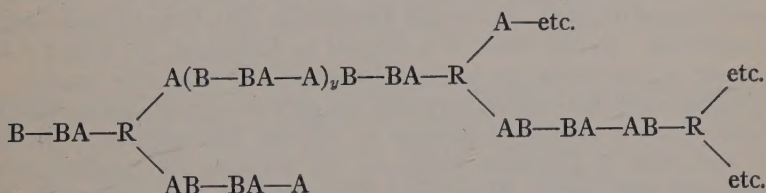
INTRODUCTION TO BRANCHED MOLECULES

By P. J. Flory

Cornell University, Ithaca, N. Y.

Non-linear polymerizations may be divided into two classes: (a) those that may lead to infinite network structures and (b) those that are incapable of doing so. By far the majority of polymerizing systems yielding non-linear molecules are of the former type. Included are the glycerol-dibasic acid condensations, the urea-formaldehyde reaction, the drying of oils, the vulcanization of rubber, and the copolymerization of a small proportion of a divinyl monomer with a vinyl monomer. In all of these examples, as well as many others which could be cited, the propagation and ramification of the polymeric structures through repeated branching or cross-linking is unlimited in the sense that, if the reaction is carried far enough, indefinitely large structures will be produced.

A simple prototype of an unlimited non-linear polymerization consists in the condensation of a polyfunctional monomer $R-A_f$, possessing $f(>2)$ functional groups of type A, with bifunctional monomers $A-A$ and $B-B$. Products obtained contain structures such as the following:



Gelation, signifying generation of an infinite structure, occurs when the reaction reaches a stage such that the *branching probability* α exceeds a critical value α_c . This branching probability α may be defined as the probability that a given chain of (zero or more) bifunctional units proceeding from a polyfunctional unit leads eventually to another branch rather than to an unreacted terminal unit. Thus, it depends essentially on the ratio of unreacted chain ends to branch points, and also on the functionality of the latter. As the condensation progresses, the number of unreacted ends diminishes and α increases toward unity as an upper limit. The critical value of α , derived under the assumption of an exclusively intramolecular reaction is given by

$$\alpha_c = 1/(f - 1) \quad (1)$$

The corresponding relation for the critical point in the random crosslinking of otherwise linear polymer molecules is

$$\rho_c = 1/(\bar{y}_w - 1) \quad (2)$$

where \bar{y}_w is the weight average degree of polymerization of the linear *primary molecules* and ρ is the fraction of the units which are crosslinked; ρ_c is the critical crosslinking density at incipient formation of an infinite network.

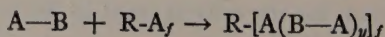
Polymer chemists continue to prefer molecules as subjects for their investiga-

tions, hence the infinite network polymers, which are characteristic of the preponderance of non-linear polymeric substances, have received much less attention than is warranted by their importance as chemical structures. To be sure, the inherent insolubility of crosslinked networks forestalls application of most physico-chemical techniques and, for this reason, they may appear less attractive to the experimentalist. A need for development of methods applicable to these insoluble structures is indicated.

In keeping with the current trend, the title of this monograph specifies *molecules*, and thus excludes the infinite network structures for which the term "molecule" is inappropriate. The main justification for mentioning unlimited non-linear polymerizations lies in pointing out how difficult it is to obtain, by most of the obvious methods for introducing non-linearity, samples suitable for investigation of the effects of non-linearity in polymer molecules. EQUATIONS (1) or (2) above show that only a very small proportion of branching points, or of cross-linkages, is required to cause gelation (*i.e.*, infinite network formation) if the linear chain length is great. Thus, gelation intervenes before the number of polyfunctional units (or of cross-linkages) can be made sufficient to introduce marked departures from linearity in the average molecular pattern. At the same time, the molecular weight distribution becomes extremely broad. Observed changes in physical behavior are more likely to result directly from the broadening of the molecular weight distribution than from the non-linearity of the molecules. In any event, it is difficult to distinguish the effects of non-linearity *per se* from those due to the heterogeneity in molecular weight.

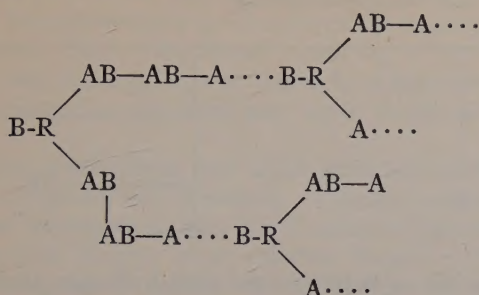
The largest molecules existing very near the gel point are, of course, decidedly non-linear, hence it should be possible by efficient fractionation to isolate a sample consisting of molecules which, on the average, may contain several polyfunctional units each. Zimm (and Thurmond) in this monograph, page 332, have followed this procedure. Serious difficulties are involved, however. In the first place, since the molecular weight distribution is extremely broad, any reasonably sharp fraction consisting of molecules large enough to contain an average of a considerable number of branches must necessarily comprise a very small percentage of the total polymer. In addition to the burden thus placed on the fractionation procedure, there is the further difficulty arising from the fact of varying degrees of non-linearity result in differences in solubility, and the fractional separation will not therefore be on the basis of molecular weight alone.

Non-linear condensation polymers may be prepared without incidence of gelation by condensing an A—B type monomer (*e.g.*, an ω -amino acid) with a polyfunctional reactant of the type R-A_f (*e.g.*, a polybasic acid)



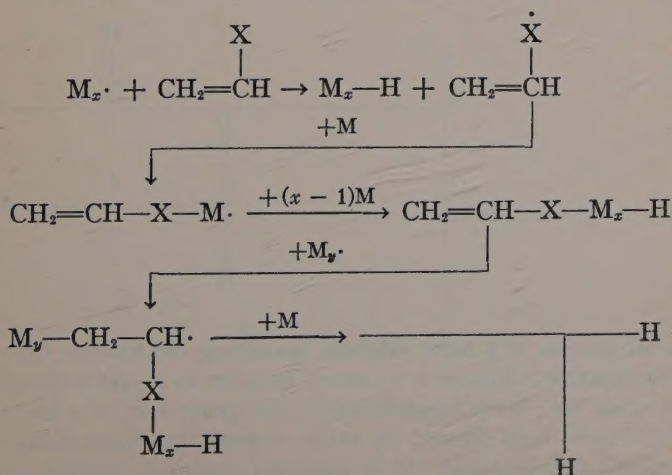
The resulting *multichain polymers* (Schaeffgen, 1948) consist of molecules each of which has exactly one polyfunctional unit. Inasmuch as all of the terminal groups are A's, two such molecules cannot condense with one another, hence the coalescence of structures required for unlimited growth is impossible. The molecular weight distribution is narrower than is obtained by ordinary linear polycondensation.

Another scheme consists in the use of an B-R-A_{f-1} polyfunctional reactant with an A—B monomer. The resulting randomly branched polymer molecules are of the following type when $f = 3$

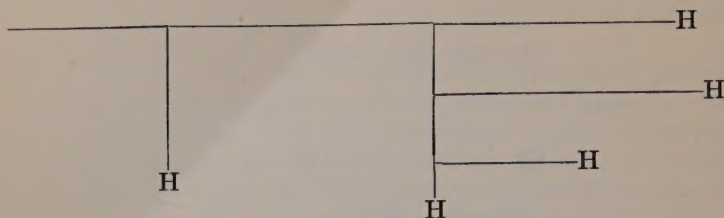


Each molecule possesses a single unreacted B group, which endows it with the capacity to link with other molecules. The critical condition (2) cannot be reached, however, as may be shown by formulating the branching probability for this case. The number of branches is variable from one molecule to another, and the molecular weight distribution consequently is broad. The natural carbohydrate polymers, amylopectin (Beckmann) and dextran (Wales), have structures resembling this pattern.

In the polymerization of vinyl monomers, there are at least two possible ways in which branching may be introduced through side reactions. Each depends primarily on a chain transfer process, the one with monomer, the other with previously formed polymer. Chain transfer by removal of an atom (*e.g.*, hydrogen) or group from a monomer molecule will be followed by the formation of a polymer molecule bearing an unsaturated terminal group, which may be combined as one of the units entering into the subsequent growth of another molecule. The sequence of reactions is indicated below,

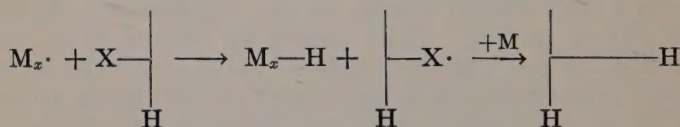


where M represents the monomer $\text{CH}_2=\text{CHX}$. Repetition of the above process, sometimes with addition of the terminal unsaturated units of several polymer molecules in the lattermost growth step, may lead to more highly branched structures like the one following:

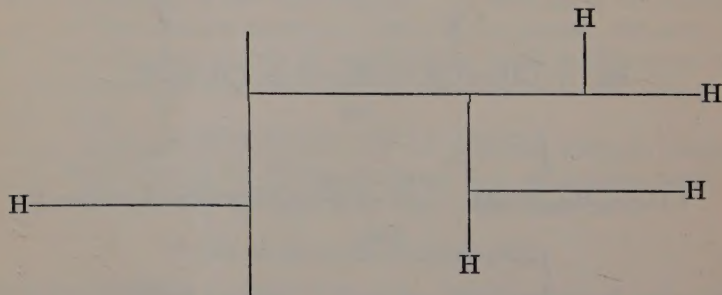


where designation of the ends terminated with hydrogen atoms acquired by chain transfer serves to indicate the directions of growth of the individual chains. Since each occurrence of chain transfer to monomer produces one permanent chain end, and also one unsaturated terminal unit which *may* subsequently be incorporated as a branch, the above scheme cannot produce branches in excess of the number of molecular ends. Hence, the branching probability cannot exceed the critical value, one-half. Formation of infinite structures is therefore impossible by the above mechanism. The similarity in structural pattern to molecules formed by condensation of B-R-A_{f-1} and A-B monomers is obvious.

Chain transfer with polymer according to the following mechanism,



may eventually lead to more highly branched structures, *e.g.*,



The over-all process is a more efficient branching mechanism than is chain transfer to monomer, inasmuch as every transfer to a polymer unit, besides forming a chain end, leads immediately to the generation of a branch. Considering the chain ends formed by other process (by chain initiation or by transfer to other substances), it is apparent that the number of branches

ordinarily will be less than the number of ends. Hence α cannot exceed the critical value one-half, without the assistance of reactions other than the ones shown. Fox, in this monograph, has shown, however, that termination by coupling of pairs of polymer radicals may, under certain circumstances, serve the function of a supplementary process providing for molecular coalescence to infinite structures. Thus, the molecule consisting of two branched structures coupled in this manner may be re-activated by subsequent transfer reactions, and a polymer radical so produced may again couple with another polymer radical, *etc.*

Both branching mechanisms may occur simultaneously in the same polymerization [*e.g.*, vinyl acetate (Wheeler)]. Usually, however, transfer to polymer is the more important process [vinyl acetate (Wheeler); methyl acrylate (Fox); polyethylene (Rugg); vinyl chloride (Rugg); 1,3 dienes (Morton)]. Owing to the variation in number of branches per molecule, the molecular weight distribution will be broadened to a marked degree by either branching mechanism.

As already pointed out, mechanisms leading to restricted branching, *i.e.*, those which do not generate infinite structures, are to be preferred for the preparation of products with a sufficient degree of non-linearity to be of interest for studies of the effects of branching on molecular properties. Quantitative definition of the degree of branching may be experimentally difficult, however, even under the most favorable circumstances. Theoretical treatment of the viscosity and solution thermodynamic properties (Stockmayer) is likewise difficult. A few bold attempts at the interpretation of the properties of branched molecules nevertheless have led to promising results (Stockmayer, Wales).

PHYSICAL PROPERTIES OF SOLUTIONS OF BRANCHED POLYMERS

By Bruno H. Zimm

General Electric Research Laboratory, Schenectady, N. Y.

The principal physical difference between branched and unbranched polymer molecules lies in the smaller spatial extension of the former at a given molecular weight. This affects their solution properties, particularly viscosity number (intrinsic viscosity) and mean square radius as measured by light scattering. The theory of the mean square radius was worked out by W. H. Stockmayer and the author a few years ago.¹ It is discussed in more detail in the following paper. Here we need only note the principal result: the mean square radius R^2 is diminished by a factor g when branch units are introduced into a molecule, the factor g being a function of the number of branch units and their distribution in the molecule.

An experimental study of these variables was carried out by C. D. Thurmond and the author at the University of California.² The system used was polystyrene with divinylbenzene added to produce tetrafunctional branch units.

It was found that the mean square radius varied with the calculated degree of branching, but that the polydispersity of the materials with respect to molecular weight, even after fractionation, obscured the picture. The weight average molecular weight was measured by light scattering, but the mean square radius was a higher average ("z-average") so that no relation could be made between the two quantities without knowledge of the molecular weight distribution, which was not known precisely.

On the other hand the viscosity number is itself a weight average quantity so that the relation between it and molecular weight should be relatively insensitive to the molecular weight distribution. Some theory was required, however, to relate the viscosity number to the number of branch units. About this time, Flory and Fox³ made their proposal that the viscosity number for high polymers was proportional to the quotient of the three-halves power of the mean square radius and the molecular weight. If this were true, it would be a simple matter to use the known relations between molecular weight, branching, and mean square radius together with the measured viscosity and molecular weight to get the number of branch units per molecule.

The experimental results showed that branching could indeed be detected and at least semi-quantitatively determined in this way. There were some quantitative discrepancies, however, whose origin is still uncertain. These were: a lack of agreement between theory and experiment for the number of crosslinks at gelation; a minor difference in form between the experimental and theoretical relations between molecular weight and viscosity number in a series of fractions from one polymerization; and variation of the Flory-Fox proportionality constant with solvent. Since further progress in this field will involve the clearing up of these three points, we discuss them briefly.

The gelation theory of Flory⁴ and Stockmayer⁵ predicts that, at gelation, the weight average number of tetrafunctional branch units per molecule should be infinite. Actually it appeared to be only 0.683 in the styrene-divinylbenzene copolymer from the viscosity and molecular weight measurements. This corresponds to gelation at an extent of reaction that is 40 per cent of the theoretical. The discrepancy, which is as yet unexplained, could arise from defects in either the gelation theory or in the calculation of the number of branch-units from the measurements. The gelation theory has been shown to give a very good account of certain condensation polymerizations⁴ and even of vinyl polymerizations,⁶ provided the fraction of branching agent is small enough.

The second difficulty is a difference between the experimental and theoretical viscosity number-molecular weight curves. The experimental curve shows less curvature than the theoretical, the high molecular weights appearing to have fewer branch units than the theory demands. The difference could be caused by an uneven segregation of material among the fractions with the highly branched molecules appearing with unbranched molecules of lower molecular weight rather than with unbranched molecules at the same molecular weight level. This is pure supposition, however.

The third difficulty is concerned with the nature of the relation between the viscosity number and the molecular weight and shape. According to Flory's hypothesis, which we have used, the viscosity number, $[\eta]$, is proportional to the quotient of the three-halves power of the mean square radius and the molecular weight. If this is true, the quantity $M[\eta]/(R^2)^{3/2}$ should be a constant for any given polymeric material in different solvents as $[\eta]$ and R^2 vary. The solvent variation of $M[\eta]/(R^2)^{3/2}$ may be obtained for ten different polystyrene fractions in several solvent pairs from the data in reference.¹ There is a marked variation of $M[\eta]/(R^2)^{3/2}$, the quantity becoming smaller as the solvent becomes better thermodynamically. This is true for all except one of the twenty-four pieces of data available. The experiments therefore cast doubt on the exactness of the proportionality between $[\eta]$ and $M/(R^2)^{3/2}$, and hence on the correctness of the values of the numbers of branch units calculated by the use of the viscosity-molecular weight relation. If this method of determining branch units is to be used for purposes requiring precise numbers, further study must be made of the viscosity-molecular weight relation.

References

1. ZIMM, B. H. & W. H. STOCKMAYER. 1949. *J. Chem. Phys.* **17**: 1301.
2. THURMOND, C. D. & B. H. ZIMM. 1952. *J. Polymer Sci.* **8**: 477.
3. FLORY, P. J. & T. G. FOX. 1950. *J. Polymer Sci.* **5**: 745.
4. FLORY, P. J. 1947. *J. Am. Chem. Soc.* **69**: 2893.
5. STOCKMAYER, W. H. 1944. *J. Chem. Phys.* **11**: 45.
6. WALLING, C. 1945. *J. Am. Chem. Soc.* **67**: 441.

DILUTE SOLUTIONS OF BRANCHED POLYMERS*

By Walter H. Stockmayer and Marshall Fixman

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

1. Introduction

In an earlier era of high polymer chemistry, branching not infrequently served as a whipping boy to explain deviations from an expected physical behavior^{1, 2} often without any independent or clear-cut evidence for the occurrence of chemical reactions leading to branched molecular structures. Today, it is clear from the general nature of the chain transfer reaction that high-conversion vinyl polymers (at least if prepared by free-radical initiation) contain more or less highly branched molecules. A sounder and more quantitative attack on the question of branching is therefore mandatory on both experimental and theoretical fronts.

From the theoretical point of view, two general problems related to branching then confront us. The one concerns the mechanism and kinetics of the branch-producing reactions and ultimately the distribution of molecular weights and degrees of branching in samples prepared under specified conditions, and is illustrated by other papers^{3, 4} in this symposium. The other concerns the effect of branching on observable physical properties, and forms the subject of this paper. It will be apparent from the previous contribution⁵ that in experimental studies of branching these two problems are not so easily separable.

Our remarks are confined almost entirely to the properties of dilute solutions. It is not intended thereby to imply that the properties of polymers in bulk are insensitive to branching; on the contrary, the known or possible influences of branching on bulk properties furnish a strong practical impetus for thorough study of the subject. It seems likely, however, that a firm theoretical understanding can be more easily and quickly attained for the properties of dilute polymer solutions than for those of the bulk materials. The properties to be discussed in the following sections are derivable from measurements of osmotic pressure, light scattering, sedimentation, diffusion and viscosity. The type of molecular structure considered is that of rather long branches, such as might occur through chain transfer reactions or copolymerization with polyfunctional monomers. Shorter, regularly spaced branches on a main backbone, such as the alkyl side groups in polyvinyl stearate, will not be treated.

2. Mean Square Radius

It has been amply shown elsewhere⁶ how the mean square radii of polymer molecules can be obtained from the angular dependence of scattered light from dilute solutions. For a molecule consisting of N chain elements (which we shall also call "segments") this quantity, which we generally denote simply by R^2 without brackets, is defined by

$$R^2 \equiv \sum_i \langle r_i^2 \rangle / N, \quad (2.1)$$

* This work has been supported by the Office of Ordnance Research under Contract No. DA-19-020-ORD-1545.

where $\langle r_i^2 \rangle$ is the mean square distance of element i from the molecular center of mass, or equally well by

$$R^2 \equiv \sum_i \sum_j \langle r_{ij}^2 \rangle / 2N^2, \quad (2.2)$$

in which $\langle r_{ij}^2 \rangle$ is the mean square distance between elements i and j . If the chains constituting the polymer molecule are long and are assumed to obey random flight statistics, R^2 can be calculated for any specified structure. An elegant general method of performing this calculation was given by Kramers⁷ and has been applied to various kinds of more or less randomly branched molecules.⁸ The results of the latter work are given in terms of a dimensionless ratio

$$g = R^2/R_0^2, \quad (2.3)$$

where R_0^2 is the mean square radius of an unbranched molecule of the same molecular weight as the branched molecule under consideration. On the basis of these calculations, light scattering would seem to afford a well-founded and rather direct means for the detection of branching. The work of Thurmond and Zimm⁹ discussed in the previous article,⁵ illustrates the application of this method, and we shall simply contribute a few remarks:

(a) The method based on light scattering measurements alone is limited experimentally to a bounded range of molecular weights. The necessity of extrapolating the angular function⁶ $P(\vartheta)$ to zero scattering angle as well as to infinite dilution places an upper limit on the molecular weights that can be studied. The scattering from dust-free dilute solutions must be measured at small angles. Here we may expect further experimental advances. For low molecular weights, however, the angular dependence of the scattering becomes very small for visible light, and there seems to be no prospect of imminent extension into the far ultraviolet. Unfortunately, the range of molecular sizes at present thus inaccessible covers a large part of that usually of practical interest.*

(b) Even in the accessible range of sizes, the method gives a result for R^2 in which the larger molecules in a sample have undesirably greater weight. Specifically, the measurements give^{6, 8} a "z-average" value,

$$\langle R^2 \rangle_z = \sum_k c_k M_k R_k^2 / \sum_k c_k M_k, \quad (2.4)$$

where c_k and M_k are weight concentration and molecular weight of molecular species k . At the same time, the data yield a weight-average molecular weight. The results therefore require a fair knowledge of the distribution of species within the sample in order to be uniquely interpreted. For unfractionated samples, at least a partial solution of the first general problem quoted in our introduction is thus required. Presumably this would not be necessary for highly fractionated samples, but it has been seen⁵ that even a very thorough fractionation scheme⁹ may not be adequate. We, therefore, feel that the most

* We are aware of the fact that small-angle X-ray scattering can give information about the radii of smaller molecules, but rather concentrated solutions must be used to get sufficient intensity. Thus the method is best suited to compact rigid molecules such as the globular proteins. For flexible chains, intermolecular interference would present a greater complication.

valuable results by the light-scattering method will come from applications to systems for which the distribution problem has been adequately solved.

(c) The calculations of g are restricted to cases in which the assumption of random-flight statistics can be made; that is, to certain special solvents. It can be shown that when the osmotic second virial coefficient A_2 is zero,⁸ or when the solvent is just at the precipitation temperature for a solute of infinite molecular weight¹⁰ ("theta-solvent"), this assumption is valid. Such solvents may not be readily available, and it is pertinent to ask how much the deviations from random-flight behavior (usually called the "excluded volume effect") will affect the values of g in better solvents. Since the excluded volume effect is a thorny problem even for linear chains, only a rough answer to the question can be given. We have recently developed some general relations concerning this effect¹¹ with which we can treat a special example. For linear chains of N elements, we find, as a first approximation,

$$R_0^2 = (Na^2/6)(1 + 1.28z + \dots); \quad z = (3/2\pi a^2)^{3/2}\beta N^{1/2}, \quad (2.5)$$

where a is the effective length of a link between chain elements in the random-flight chain and β is the "excluded volume" between a single pair of elements (proportional to $\psi_1(1 - \Theta T^{-1})$ in the Flory notation¹⁰). This result has also been obtained by others.¹² It gives only the first terms of an alternating series which does not converge very rapidly, but it should serve as an indication. Applying the same method to a cruciform molecule with four branches of equal length, we obtain

$$R^2 = (g_0 Na^2/6)(1 + 1.12z + \dots) \quad (2.6)$$

where g_0 , the random-flight ratio of R^2 to R_0^2 , is equal to $5/8$ for this particular molecular model. Since z is positive when A_2 is positive, this suggests that for a given molecular weight the initial volume effect is slightly greater for the linear chains. If we compare linear and branched molecules having the same value of R^2 in a theta-solvent, however, we see that on going to a better solvent the volume effect will be somewhat greater for the branched molecule. At any rate, these calculations indicate that the effect on R^2/R_0^2 is not nearly as serious as one might have feared and, therefore, that results of considerable significance may be derived from measurements in good solvents. The experimental data⁹ are scarcely conclusive on this point. The details of the above calculation will not be given here.

(d) We can show by an example that a more detailed study of the angular dependence of scattered light intensity, *e.g.* of the curvature of the reciprocal scattering function⁶ $P^{-1}(\vartheta)$, is not likely to yield significant information about branching. If we express the scattering function by

$$P(\vartheta) = 1 - (k^2 s^2 R^2/3) + (B k^4 s^4 R^4/12) - \dots, \quad (2.7)$$

$$ks = (4\pi/\lambda) \sin(\vartheta/2)$$

then for cruciform molecules with f branches of equal length we get (for random-flight statistics)

$$B = f(7f - 6)/(3f - 2). \quad (2.8)$$

Since B decays from unity for linear chains ($f = 1$ and 2) only to $7/9$ for large f , this small change is easily overshadowed by the effects of molecular weight distribution.⁶ In view of this fact we again give no details.

The concentration dependence of light scattering is considered together with that of osmotic pressure in a later section.

3. Mean Segment Density

Although the effect of branching on the angular dissymmetry of light scattering is essentially restricted to its effect on the mean square radius of the molecules, this will not necessarily be true of other dilute-solution properties. For this reason, it is instructive to examine the average density $\rho(r)$ of chain segments as a function of distance r from the molecular center of mass. This function, while of course not directly observable, serves as the starting point for some theories relating to the osmotic second virial coefficient¹³ or to hydrodynamic properties.¹⁴ In this section we accordingly calculate $\rho(r)$ for certain special examples of branched structures, again under the restriction that the chains are long and that random-flight statistics are valid.

Details of the calculations are described in Appendix A (see page 347). It is there shown that the mean density is simply

$$\rho(r) = \sum_n W_n(r), \quad (3.1)$$

where $W_n(r)4\pi r^2 dr$ represents the probability that element n is in an infinitesimal spherical shell at a distance r from the center of mass. The calculation of W_n for any segment on a specified molecule reduces to a standard problem in probability. For the linear chain, the results have been given by Isihara¹⁵ and independently by Debye and Bueche.¹⁶

Each of the functions W_n is a normal distribution

$$W_n(r) = \pi^{-3/2} C_n^{-3} \exp(-C_n^{-2} r^2); \quad C_n^{-2} = 2 \langle r_n^2 \rangle / 3, \quad (3.2)$$

where $\langle r_n^2 \rangle$ is the mean square distance of segment n from the center of mass. For cruciform molecules with f branches of arbitrary lengths, N_α, N_β, \dots , we find

$$\langle r_n^2 \rangle^{(\beta)} / a^2 = n(1 - 2N_\beta N^{-1}) + n^2 / N + \sum_\alpha N_\alpha^3 / 3N^2 \quad (3.3)$$

for the n^{th} segment from the branch point on chain β . Here a is the length of a link between segments, and $N = \sum_\alpha N_\alpha$.

As a numerical example we have evaluated $\rho(r)$ for the tetrafunctional cruciform molecule with all branches of equal length. FIGURE 1 shows the results (curve B) in reduced form, the dimensionless ordinate $R^3 \rho / N$ being plotted against r/R , where R is the root-mean-square radius. For comparison, the same function is plotted for the linear chain (curve L). It is seen that except at small distances the two functions are quite similar. They cross at approximately $r/R = 0.57$ and 1.27 . For the branched molecule considered, however, g is $5/8$, which means that it must have a molecular weight $8/5$ times that of a linear molecule with the same mean square radius. Thus, if we plot unreduced values of $\rho(r)$ the results look quite different, as in FIGURE 2, where curve B again represents the branched molecule, and curve L a linear molecule

with the same value of R . The functions are here shown as $\log \rho$ against r^2/R^2 to illustrate the degree to which they depart from a single gaussian curve, which would be linear. It is seen that the branched molecule gives the slightly greater curvature.

Still another illustration of the same results is afforded by FIGURE 3, where we plot $r^2\rho$ against r in arbitrary units. The branched molecule conforms to

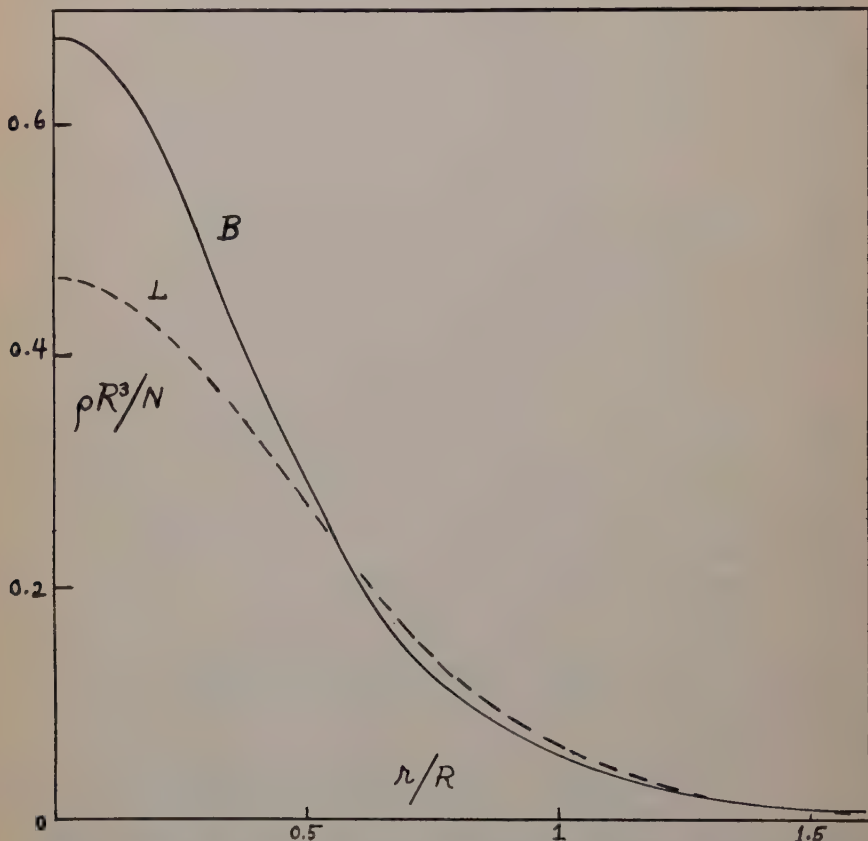


FIGURE 1. Reduced mean segment density for a cruciform branched molecule of four chains (B) and for a linear molecule (L) with the same mean square radius R^2 .

curve B, while L denotes a linear molecule with the same mean square radius as B and L' a linear molecule with the same molecular weight as B.

From a comparison of curves B and L in these figures we make two statements tentatively applicable to branched molecules in general:

(a) If a branched molecule has the same mean square radius as a linear molecule, it has everywhere a greater mean segment density. Thus, for properties which depend on the ability of two molecules to interpenetrate,¹³ or on the hydrodynamic permeability of the molecules to solvent,¹⁴ we may expect that

equality of mean square radii does not necessarily mean equality of these properties. This expectation will be amplified and confirmed in later sections.

(b) In spite of the fact that the density function does not have exactly the same shape for linear and branched molecules (FIGURE 1), the difference is

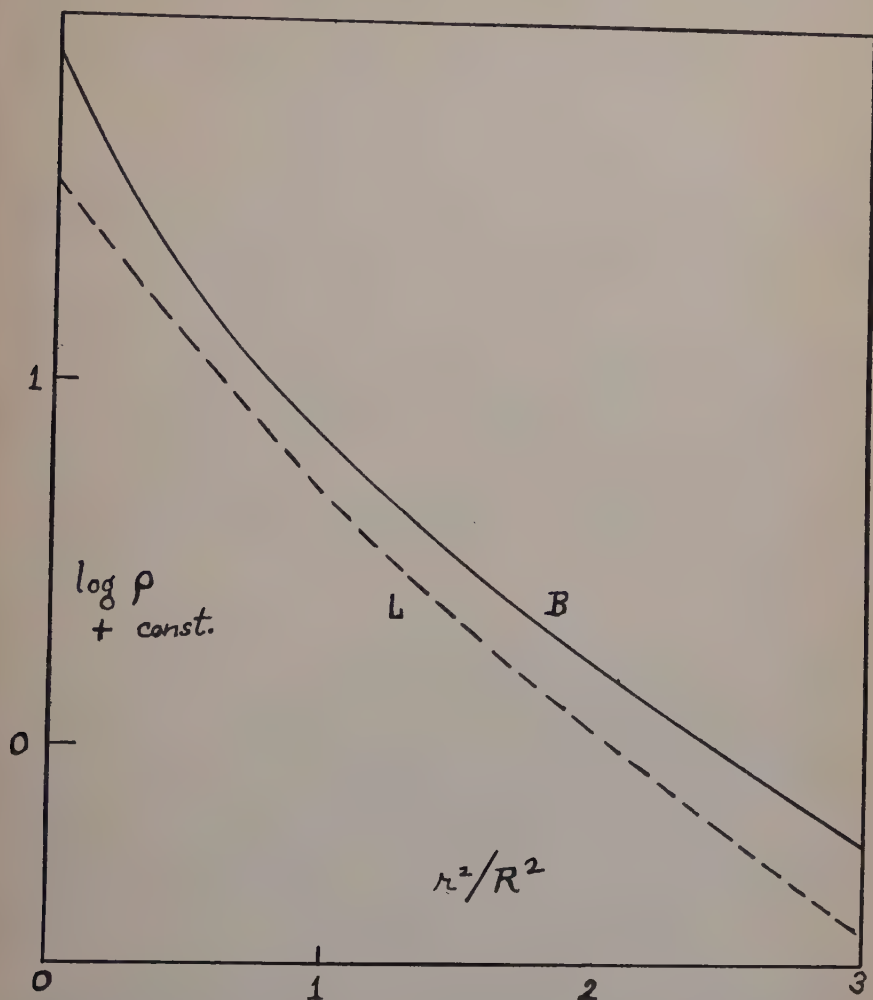


FIGURE 2. Semi-logarithmic plot of mean density for cruciform molecule (B) and linear molecule (L) with same mean square radius R^2 .

greatest for small distances, and is much less visible in FIGURE 3, where L is nearly superposed on B if the ordinates of the former are multiplied by $\frac{8}{5}$. Hence, for properties depending principally on the density at distances not too far removed from R , it will be a fairly good approximation to write

$$\rho(r) = (N/R^3)F(r/R), \quad (3.4)$$

where $F(r/R)$ is a function independent of branching.

The second statement above can be reinforced in a somewhat different way. With EQUATIONS (3.1) and (3.2) it is a simple matter to calculate the mean fourth power, $\langle R^4 \rangle \equiv \sum_n \langle r_n^4 \rangle / N$, of the distance from the molecular center of mass, and the ratio of this quantity to $\langle R^2 \rangle^2$ then gives some indication of the

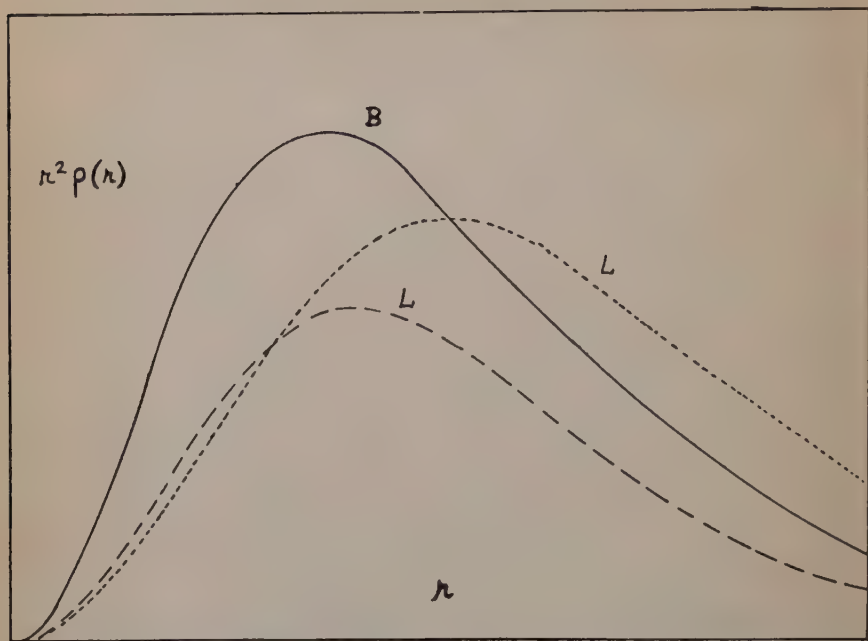


FIGURE 3. Radial distribution function $r^2 \rho(r)$ for branched molecule (B), linear molecule (L) with same value of mean square radius, and linear molecule (L') with same molecular weight. Scale is arbitrary.

shape of the mean density function. The general result is

$$\langle R^4 \rangle / \langle R^2 \rangle^2 = 15N(\sum_n C_n^{-4}) / 9(\sum_n C_n^{-2})^2, \quad (3.5)$$

which for the special case of cruciform molecules with f equal branches gives

$$\langle R^4 \rangle / \langle R^2 \rangle^2 = (12 - 30f + 20f^2) / (3f - 2)^2. \quad (3.6)$$

This ratio is just 2 for linear chains ($f = 1$ or 2), becomes 2.08 for $f = 3$, 2.12 for $f = 4$, and reaches 2.22 for large f . We have also made the calculation for a molecule with four trifunctional branch units (the "iso" form⁸) and all chains of equal length; for this case the ratio is 1.97. In contrast to these figures, the ratio for a single gaussian function is $5/3$. We may thus again conclude that the density functions for branched and linear molecules are not too dissimilar in shape, and certainly are more like each other than like a single gaussian function. Naturally there will be differences of detail, but the indications are that EQUATION (3.4) would not be too misleading.

4. Second Virial Coefficient and Solubility

The effect of branching on the thermodynamic properties of polymer solutions has not been much investigated. Although the familiar lattice theory has been applied^{17, 18} to branched molecules, no pertinent experiments on concentrated solutions are known to us, and our discussion is therefore largely concerned with dilute solutions. The quantity of interest is thus the second virial coefficient A_2 in the expansions

$$\pi/RTc = M_n^{-1} + A_2c + \dots, \quad (4.1)$$

$$Hc/\tau = M_w^{-1} + 2A_2c + \dots, \quad (4.2)$$

for osmotic pressure and turbidity, respectively. Since A_2 is only a slowly varying function of molecular weight, it is adequate for our purpose to consider a homogeneous polymer sample and ignore the complications¹⁸ introduced by polydispersity.

Qualitatively, the experimental results^{9, 19} show that, at a given molecular weight, branching lowers the value of A_2 , but no quantitative relations for this effect have been given. The several existing theories of the virial coefficient can be adapted, as indicated below, to branched molecules, although, since these are somewhat inadequate even for linear polymers, the results have limited usefulness.

Fundamentally, the second virial coefficient, describing the interaction in dilute solutions between two molecules a , b of molecular weight M , is given²⁰ by the integral

$$A_2 = (N_0/2VM^2) \int \dots \int F_1(a)F_1(b)[1 - \exp(-U_{ab}/kT)] d(a, b), \quad (4.3)$$

where N_0 is Avogadro's number, V is the (arbitrarily large) volume of infinitely dilute solution containing the two molecules, and U_{ab} is the potential of average force between them, in the chosen solvent, as a function of their complete sets of coordinates, (a) and (b) . The singlet distribution functions $F_1(a)$ and $F_1(b)$ measure the relative probabilities of the various internal configurations of the molecules, and the indicated integration extends over all possible configurations of the system of two molecules.

In applying the general equation to linear molecules, Zimm was able to give the first two terms in a polynomial:

$$A_2 = (N_0\beta/2M_0^2)(1 - 2.88z + \dots), \quad (4.4)$$

where M_0 is the molecular weight of a segment and the symbols β , z have the same significance as in EQUATION (2.5). The above two terms are the contributions arising from configurations in which one and two pairs, respectively, of segments from the two molecules are interacting with each other (*i.e.* are essentially in contact). It is easy to follow Zimm's procedure for simple branched molecules, and we have done so for cruciform molecules with branches of equal length. For example, the result for tetrafunctional cruciform mole-

cules is

$$A_2 = (N_0\beta/2M_0^2)(1 - 4.00z + \cdots), \quad (4.5)$$

which is in the expected direction of giving a smaller value of A_2 . It must be stated, however, that the above developments do not converge rapidly and that, in the usual range of molecular weights, many more terms, corresponding to more than two contacts between the molecules, are important. Therefore, the above result, though quite rigorous as far as it goes, is not quantitatively useful.

A more satisfactory result in some ways is afforded by the theory of Flory and Krigbaum.¹³ In this method, the potential of average force U_{ab} is first averaged over all configurations of the two molecules at fixed separation r of their centers of mass. This average potential $U(r)$ is then used in a final integration:

$$A_2 = (2\pi N_0/M^2) \int_0^\infty [1 - \exp(-U(r)/kT)] r^2 dr. \quad (4.6)$$

This amounts to neglecting fluctuations of the segment density from its average value.

In their theory, Flory and Krigbaum evaluate $U(r)$ on the assumption that the mean segment density is given by a single gaussian function, which may account in part for their failure to secure a quantitatively successful result for linear polymers. However this may be, the important point for us is that the result does not specifically depend on the fact that the molecules are linear. If the hypothesis of EQUATION (3.4) is adopted, the Flory-Krigbaum equation then holds for both linear and branched molecules. In our notation the result is

$$A_2 = (N_0\beta/2M_0^2)F(X); \quad X = K\beta M^2/R^3, \quad (4.7)$$

where K is a constant and $F(X)$ is a definite integral¹³ which decreases from unity to small values as X is increased. Therefore, to the extent that the theory can be fitted to data for linear polymers, it is possible to predict A_2 for branched polymers whose mean square radii can be calculated.* Since X is inversely proportional to R^3 , it is seen that branching will increase X and thus lower the value of A_2 , as expected.

Although, as mentioned earlier, there has been some application of lattice theory to solutions of branched polymers, this has not progressed to a discussion of solubility and fractionation. In view of the important effects of distribution, particularly on the light-scattering method of obtaining R^2 , a study of the fractionation of branched polymers would obviously be very desirable. Since both experiments⁹ and theory indicate that A_2 changes sign at $\beta = 0$ for both linear and branched systems, we may expect that the temperature or solvent composition for incipient precipitation of very high polymer will not be altered by branching. Concerning the phase equilibria for finite molecular weights we make no predictions. A complication that should be kept in mind

* This statement would still hold if an improved density function were used in place of the single gaussian expression. This would lead to a different function $F(X)$ but the variable X would remain the same.

is that of possible crystallinity in the precipitated polymers. If this arises, one may expect branching to reduce crystallization and thus to enhance solubility, as has, in fact, been observed.²¹

5. Hydrodynamic Properties

Of all dilute solution properties, viscosity is the one for which it would be most desirable to have a sound theoretical understanding of the effect of branching. This is principally because of the ease of experimental measurement, but also because the intrinsic viscosity is quite a sensitive function of branching. The molecular friction constant, as obtained from sedimentation or diffusion constants, is a less sensitive quantity, but because of its close theoretical connection to the viscosity we discuss them together in this section. It will be shown that previous theories require some amendment, but that a fairly satisfactory result can be attained.

According to the older theories based on the "free draining" model of the polymer molecule, intrinsic viscosity is directly proportional to the mean square radius.^{7, 22} These theories are inadequate, and later consideration^{14, 23, 24} of the hydrodynamic interference between segments ("shielding effect") showed that, in the limit of high molecular weights, the intrinsic viscosity becomes proportional to R^3/M for linear polymers. Similar treatment of the molecular friction constant^{13, 23, 24} shows that, at high molecular weights, it should become proportional to R . These theoretical results are for linear molecules obeying random-flight statistics and, accordingly, in the limit both intrinsic viscosity and friction constant are predicted to vary as $M^{0.5}$.

Several years ago, Flory and Fox²⁵ suggested that the limiting behavior was actually attained at quite low molecular weights. If this is the case, we have

$$[\eta] = \Phi'R^3/M; \quad (5.1)$$

$$F_0/\eta_0 = P'R, \quad (5.2)$$

where F_0 is the molecular friction constant (in infinitely dilute solution), η_0 the viscosity of the solvent, and Φ', P' universal constants. It is assumed that these equations hold even when R does not follow random-flight statistics and, therefore that proportionality of $[\eta]$ or F_0 to a power of M greater than 0.5 must be attributed to molecular-weight dependence of the excluded-volume effect. We are in essential accord¹¹ with this point of view. An impressive array of experimental evidence²⁶ attests to the practical success of this theory.

In view of the simplicity as well as success of the developments discussed above, it is tempting at first to adopt EQUATIONS (5.1) and (5.2) as they stand for the treatment of branched molecules as well. We should then have simply

$$[\eta] = \Phi'M^{-1}R_0^3g^{3/2}; \quad (5.1')$$

$$F_0/\eta_0 = P'R_0g^{1/2}, \quad (5.2')$$

or, on comparing the intrinsic viscosity of a branched molecule with a linear one of the same composition and molecular weight,

$$[\eta] \text{ (branched)} / [\eta] \text{ (linear)} = g^{3/2} \quad (5.1'')$$

This relationship was used by Thurmond and Zimm⁹ with qualitative success, but their results give no direct quantitative test because the true extent of branching in their samples is unknown. Indirectly, however, it appears that EQUATION (5.1'') might overestimate the effect of branching on the viscosity, for the derived degree of branching (expressed in terms of the cross-linking index γ) was appreciably lower ($\gamma = 0.41$) than that expected ($\gamma = 0.62$) from the measured molecular weights of their divinylbenzene-styrene copolymer and a pure polystyrene prepared under the same conditions. A recent study in this laboratory²⁷ of high-conversion polyvinyl acetates also showed that EQUATION (5.1'') predicts less branching than was expected from the known chain transfer constants to monomer and polymer. Measurements on branched condensation polymers in a much lower molecular-weight range^{28, 29} lead to the same conclusion.

The hydrodynamic behavior of branched polymers has been discussed by Kuhn and Kuhn,³⁰ but for high molecular weights their theory leads directly to EQUATIONS (5.1') and (5.2'), on which we have just cast suspicion. From the calculations of mean segment density presented in Section 3, it is highly plausible that the effective "hydrodynamic" radius of a polymer molecule is less sensitive to branching than is its root-mean-square radius R , since a branched molecule has everywhere a greater mean segment density than a linear molecule with the same value of R . Presumably, this could be demonstrated by either the method of Debye and Bueche¹⁴ or by that of Kirkwood and Riseman²⁴ (KR), but the former is worked out only for a model (constant mean segment density within a sphere) which is inadequate, and extensions would involve much mathematical labor.

Accordingly, we apply the KR method to the now familiar case of cruciform molecules. Since the theory of intrinsic viscosity is beset with a fundamental difficulty in treating the effects of the Brownian motion,³¹ we consider the more nearly correct and easier theory of the friction constant.* In view of the experimental validity of EQUATIONS (5.1) and (5.2) for linear polymers, we shall assume that the *ratio* of effective hydrodynamic radii of branched to linear polymers that we obtain for the friction constant can also be used to discuss the intrinsic viscosity.

Details of the KR theory for the friction constants of cruciform molecules are presented in Appendix B (see page 349). The limiting result for high molecular weights is

$$F_0/\eta_0 = (9\pi^{3/2}/4)R_0h; \quad (5.3)$$

$$h = f^{1/2}[2 - f + 2^{1/2}(f - 1)]^{-1}, \quad (5.4)$$

where f is the number of branches. When $f = 1$ or 2 , the factor h is unity, giving the KR result for linear chains. For $f > 2$, therefore, h is the ratio of the effective hydrodynamic radius of the cruciform molecule to that of a linear

* Even for the friction constant, the KR theory involves a mathematical approximation (neglect of certain fluctuation terms) of unknown validity. It has also been pointed out to us by Doctor C. M. Tchen that the Oseen perturbation formula, basic to the KR approach, must be modified if the chain elements are in relative Brownian motion. It may, however, be reasonably supposed that these effects are minor for consideration of the *relative* behavior of branched and linear molecules.

molecule of the same molecular weight. For such molecules the corresponding ratio of mean square radii is

$$g = (3f - 2)/f^2 \quad (5.5)$$

and we find, as hoped, that h is much less sensitive to branching than is $g^{1/2}$.

Although we believe that the KR theory could be worked out for more complicated branched molecules, we have not yet had the opportunity to do so. In the meantime, we can obtain useful results by making the assumption that the relation *between* h and g obtained from EQUATIONS (5.4) and (5.5) by elimination of f will hold at least approximately for branched molecules in general. Following the suggestion made earlier, we then write

$$[\eta] = \Phi' M^{-1} R_0^3 h^3, \quad (5.6)$$

which is equivalent to replacing EQUATION (5.1'') by

$$[\eta] \text{ (branched)} / [\eta] \text{ (linear)} = h^3 \quad (5.6')$$

The relation between h^3 and g obtained from EQUATIONS (5.4) and (5.5) is shown graphically in FIGURE 4. The value of g equivalent to an observed viscosity-ratio h^3 can be read from the graph, after which the extent of branching can be obtained⁸ from the value of g . This procedure leads to much more satisfactory estimates of branching than that based on EQUATION (5.1''). For the high-conversion polyvinyl acetates mentioned earlier²⁷ it gives results in good agreement (to within 20 per cent) with the kinetic values. For the styrene-divinylbenzene systems of Thurmond and Zimm,⁹ we illustrate the improvement by recalculating their results for the a fractions, shown in TABLE 1. The weight average number of branches per molecule, \bar{n}_w , is now 1.57 which gives a crosslinking index of 0.61, in excellent agreement with that expected from the observed molecular weights of their branched and unbranched polymers.

The theory and results just presented are for solvents in which random-flight statistics may be assumed. In better solvents, the experiments^{9, 27} show that h^3 is only very slightly larger than in a "theta-solvent." This has been discussed^{5, 9} in terms of a solvent effect on the supposedly universal constant Φ' but more data will be needed to settle this point. In any case, the empirical result is that a fair estimate of branching can be obtained by the above scheme even in good solvents.

Finally, we may remark that application of EQUATIONS (5.6) or (5.6') to unfractionated materials will give nearly weight-average values of h^3 and g , if weight-average molecular weights are used. This statement is based on calculations²⁷ with several different assumed distribution functions and depends, of course, on the fact that the intrinsic viscosity is itself a weight-average quantity.

Apparently, the slope of inherent viscosity against concentration also reflects the presence of branching,⁵ but attempts at theoretical discussion would be premature.

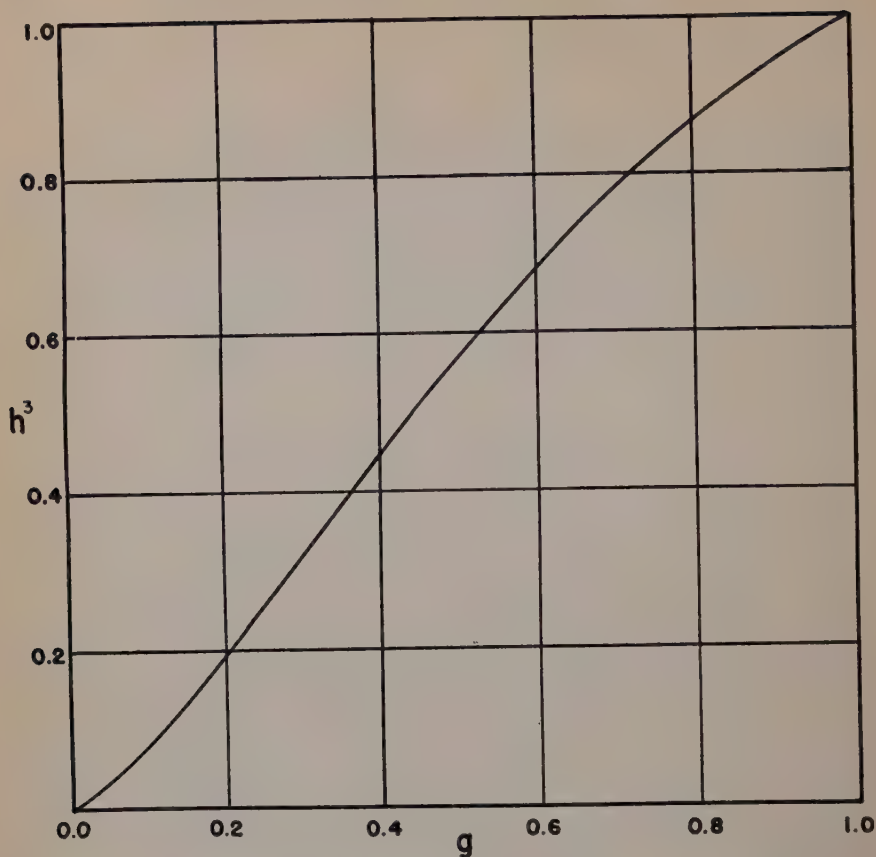


FIGURE 4. Ratio h^3 of intrinsic viscosities of branched and linear molecules of the same molecular weight, as a function of the ratio g of their mean square radii.

TABLE 1
BRANCHING OF STYRENE-DIVINYLBENZENE COPOLYMERS
(Data of Thurmond and Zimm⁹)

Fraction	$(h^3)^*$	g	\bar{M}_w
S — 1a	0.61	0.54	4.3
2a	0.76	0.68	2.2
3a	0.80	0.72	1.85
4a	0.93	0.89	0.6
5a	0.93	0.89	0.6
6a	1.0	1.0	0
Weight average			1.57

* From intrinsic viscosity in butanone-isopropanol.

6. Conclusion

Having discussed various properties of branched polymers in dilute solution, we should, logically, conclude with an opinion as to the best physical means of detecting branching quantitatively. Although the theory we have given is rudimentary and needs further development, we believe the method best combining simplicity and sensitivity is based on a combination of light scattering and viscosity measurements, the former to give the weight-average molecular weights needed for use of the viscosity relations. The extent of branching should preferably not be estimated from the curvature or slope of a double-logarithmic plot of $[\eta]$ against M_w , but from a comparison between branched and linear polymers by means of EQUATION (5.6'). The former procedure, though sound in principle,⁸ requires measurements of too great precision. If at all possible, the viscosity measurements should be made in a "theta solvent," although, empirically, the results in other solvents are not too different.

Empirically, of course, any property sufficiently sensitive to branching could be used for control purposes, but since most such properties also depend on molecular weight the results may not be unique. Moreover, the comparison of two different properties that depend on branching may reveal nothing. Thus, for example, for certain polyesters Weil²⁹ found that melt viscosity and intrinsic viscosity are both decreased by branching, but in such a way that a plot of one property against the other gives a single curve for both linear and branched samples; and Baker²¹ similarly found that comparisons between cloud points and intrinsic viscosities gave no clue to branching.

Many more careful experiments are needed on polymers with known degrees of branching (and, if possible, known distributions!). Coupled with further attempts to extend the existing theory, these will provide considerable progress toward the objectives outlined at the start.

Appendix A. Mean Segment Density

Let a polymer molecule consist of N elements or segments, which in an instantaneous configuration are located at positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \dots$ relative to the molecular center of mass. Any one of these position vectors can be expressed as a sum over the set of bond vectors σ_i specifying the direction of each of the skeletal bonds between segments:

$$\mathbf{r}_n = \sum_{i=1}^N \lambda_{ni} \sigma_i. \quad (\text{A.1})$$

The λ_{ni} are numerical coefficients which can be found quite easily for simple structures.

Since we assume the chains composing the molecule to obey random-flight statistics, the bond vectors have the properties

$$\sigma_i^2 = a^2; \quad \langle \sigma_i \cdot \sigma_j \rangle = 0; \quad (\text{A.2})$$

that is, the bonds have a length a and are connected to each other by unre-

stricted universal joints. From EQUATIONS (A.1) and (A.2) we have

$$\langle r_n^2 \rangle = a^2 \sum_i \lambda_{ni}^2. \quad (\text{A.3})$$

We now ask for the probability $W_n(\mathbf{r}_n)d\mathbf{r}_n$ that the n^{th} element lies in the volume element $d\mathbf{r}_n$ at \mathbf{r}_n , irrespective of the positions of all other elements. Since by EQUATION (A.2) the bond vectors form a set of random quantities, and since by EQUATION (A.1) the position vector \mathbf{r}_n is linear sum over this set, we may write³² at once

$$W_n(\mathbf{r}_n) = (C_n^3/\pi^{3/2}) \exp(-C_n^2 r_n^2); \quad C_n^{-2} = 2 \langle r_n^2 \rangle / 3, \quad (\text{A.4})$$

provided the chains are sufficiently long.

The average segment density can now be easily found in terms of the functions W_n . In any instantaneous configuration, the density at a point \mathbf{r} will be given by the discontinuous function

$$\rho_{\text{inst.}}(\mathbf{r}) = \sum_n \delta(\mathbf{r} - \mathbf{r}_n), \quad (\text{A.5})$$

where the delta-functions are so normalized that

$$\int \delta(\mathbf{r} - \mathbf{r}_n) d\mathbf{r}_n = 1. \quad (\text{A.6})$$

The average density $\rho(\mathbf{r})$ is then seen to be

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_n \int \delta(\mathbf{r} - \mathbf{r}_n) W_n(\mathbf{r}_n) d\mathbf{r}_n \\ &= \sum_n W_n(\mathbf{r}). \end{aligned} \quad (\text{A.7})$$

In view of EQUATIONS (A.3) and (A.4), the task of computing $\rho(\mathbf{r})$ for any particular molecule thus reduces essentially to that of specifying the coefficients λ_{ni} of EQUATION (A.1), and we proceed to do this for several examples.

Consider first the case of a cruciform molecule, with f branches of lengths $N_1, N_2, \dots, N_\alpha, \dots, N_f$ issuing from a single branch unit. The position $\mathbf{x}_n^{(\alpha)}$ of element n on branch α , relative to the branch unit as origin, is simply the sum of all the bond vectors $\sigma_i^{(\alpha)}$ along this branch from the branch point to element n :

$$\mathbf{x}_n^{(\alpha)} = \sum_{i \leq n} \sigma_i^{(\alpha)}. \quad (\text{A.8})$$

The location \mathbf{X} of the center of mass relative to the branch point is given by

$$\mathbf{X} = \sum_\alpha \sum_{n=1}^{N_\alpha} \mathbf{x}_n^{(\alpha)} / N, \quad (\text{A.9})$$

where $\sum_\alpha N_\alpha = N$. Thus, the position of element n on branch β , relative to the center of mass, is

$$\mathbf{r}_n^{(\beta)} = \mathbf{x}_n^{(\beta)} - \mathbf{X} = \sum_\alpha \sum_i \lambda_{ni}^{(\alpha)} \sigma_i^{(\alpha)}, \quad (\text{A.10})$$

where

$$\begin{aligned}\lambda_{ni}^{(\alpha)} &= 1 - N^{-1}(N_\beta - i) \text{ for } \alpha = \beta, i \leq n; \\ &= N^{-1}(N_\alpha - i) \quad \text{for } \alpha = \beta, i > n, \\ &\quad \text{and } \alpha \neq \beta, \text{ all } i.\end{aligned}$$

Using these expressions for the λ_{ni} in EQUATION (A.3) and replacing sums by integrals, we get

$$\langle r_n^2 \rangle^{(\beta)} / a^2 = n(1 - 2N_\beta N^{-1}) + n^2/N + \sum_\alpha N_\alpha^3 / 3N^2. \quad (\text{A.11})$$

As a check at this point, we may compute the mean square radius:

$$R^2 = N^{-1} \sum_\beta \int_0^{N_\beta} \langle r_n^2 \rangle^{(\beta)} dn = a^2 N^{-1} \sum_\beta (N_\beta^2/2 - N_\beta^3/3N), \quad (\text{A.12})$$

which is a result previously given.⁸

The mean density for any cruciform molecule may now be found by using EQUATION (A.11) in (A.4). As a numerical example, we select the tetrafunctional cruciform molecule with all branches of equal length, for which the equations become

$$\begin{aligned}\rho(r) &= 4\pi^{-3/2} \sum_{n=0}^{N/4} C_n^3 \exp(-C_n^2 r^2); \\ C_n^{-2} &= (Na^2/72)(1 + 6\eta + 3\eta^2); \\ \eta &= 4n/N,\end{aligned} \quad (\text{A.13})$$

or, on replacing the sum by an integral,

$$\begin{aligned}\rho(r) &= N\pi^{-3/2} \int_0^1 C^3 \exp(-C^2 r^2) d\eta; \\ C^{-2} &= (2R^2/15)(1 + 6\eta + 3\eta^2),\end{aligned} \quad (\text{A.14})$$

since for this molecule $R^2 = 5Na^2/48$.

The other results given in Section 3 follow by obvious extensions of the examples quoted above, and it seems unnecessary to give further details.

Appendix B, Friction Constant of Cruciform Molecules

According to Kirkwood and Riseman,²⁴ the friction constant of a polymer molecule is given by

$$F_0 = \zeta \sum_i \psi_i, \quad (\text{B.1})$$

where ζ is the friction constant of a single chain element and the quantities ψ_i for each segment are to be found from

$$\psi_i = 1 - (\zeta/6\pi\eta_0) \sum_{s \neq i} \langle r_{si}^{-1} \rangle \psi_s. \quad (\text{B.2})$$

In this equation, η_0 is the solvent viscosity and $\langle r_{sl}^{-1} \rangle$ is the mean reciprocal distance between elements s and l . For the physical basis of this theory the reader is referred to the original article.²⁴

For chains obeying random-flight statistics and having an effective link length b between segments, the mean reciprocal distances are given by

$$\langle r_{sl}^{-1} \rangle b = (6/\pi)^{1/2} |l - s|^{-1/2} \quad (\text{B.3})$$

With this relation, EQUATION (B.2) may be changed into an integral equation (valid for long chains) which can be solved. Here we consider cruciform molecules, composed of N segments in all, with f branches each of N/f segments. For this case the integral equation corresponding to (B.2) is

$$\psi(x) = 1 - \lambda \int_0^1 K(x, t) \psi(t) dt; \quad (\text{B.4})$$

$$K(x, t) = |x - t|^{-1/2} + (f - 1)(x + t)^{-1/2},$$

where the parameter λ is given by

$$\lambda = \zeta N^{1/2} / (6\pi^3)^{1/2} b \eta_0 f^{1/2}. \quad (\text{B.5})$$

The solution of EQUATION (B.4) follows that given by KR in all respects. With the definitions

$$\psi_0 = \int_0^1 \psi(x) dx, \quad \varphi(x) = \psi(x) - \psi_0, \quad (\text{B.6})$$

we obtain from (B.4) a new equation

$$\varphi(x) = f(x) - \lambda \int_0^1 K(x, t) \varphi(t) dt, \quad (\text{B.7})$$

where

$$f(x) = 1 - \psi_0 \mu(x); \quad (\text{B.8})$$

$$\mu(x) = 1 + \lambda \int_0^1 K(x, t) dt \quad (\text{B.9})$$

The kernel $K(x, t)$ may be expressed as

$$K(x, t) = \pi^{-1/2} \int_{-\infty}^{\infty} e^{-\beta^2 |x-t|} d\beta + (f - 1) \pi^{-1/2} \int_{-\infty}^{\infty} e^{-\beta^2 (x+t)} d\beta. \quad (\text{B.10})$$

If this is used in EQUATION (B.7) and the order of integration changed (which is here permissible), the equation becomes

$$\varphi(x) = f(x) - \lambda \pi^{-1/2} \int_{-\infty}^{\infty} g(x, \beta) d\beta, \quad (\text{B.11})$$

where

$$g(x, \beta) = \int_0^1 [e^{-\beta^2 |x-t|} + (f - 1)e^{-\beta^2 (x+t)}] \varphi(t) dt. \quad (\text{B.12})$$

This function, like the analogous one of KR for linear chains, satisfies the differential equation

$$\partial^2 g / \partial x^2 = \beta^4 g - 2\beta^2 \varphi. \quad (\text{B.13})$$

Since these functions are desired in the interval $0 \leq x \leq 1$, we may use Fourier series

$$\begin{aligned} \varphi(x) &= \sum_{k \geq 0} \varphi_k \cos \pi k x, & f(x) &= \sum_{k \geq 0} f_k \cos \pi k x, \\ g(x, \beta) &= \sum_{k \geq 0} g_k(\beta) \cos \pi k x \end{aligned} \quad (\text{B.14})$$

EQUATION (B.13) then gives

$$g_k(\beta) = 2\beta^2 \varphi_k / (\beta^4 + \pi^2 k^2), \quad (\text{B.15})$$

and from EQUATION (B.11) we obtain

$$\varphi_k = f_k - \lambda \pi^{-1/2} \int_{-\infty}^{\infty} g_k(\beta) d\beta. \quad (\text{B.16})$$

Now from EQUATIONS (B.6) and (B.14) we have

$$\varphi_0 = \int_0^1 \varphi(x) dx = 0,$$

so that EQUATIONS (B.15) and (B.16) give

$$g_0(\beta) = 0; \quad f_0 = 0.$$

But this means that

$$\int_0^1 f(x) dx = f_0 = 0,$$

so that from EQUATION (B.8) we recover

$$0 = 1 - \psi_0 \int_0^1 \mu(x) dx, \quad (\text{B.17})$$

which can be rewritten from EQUATION (B.9) as

$$\begin{aligned} 1/\psi_0 &= 1 + \lambda \int_0^1 \int_0^1 K(x, t) dx dt \\ &= 1 + (8\lambda/3)[2 - f + 2^{1/2}(f - 1)] \end{aligned} \quad (\text{B.18})$$

The friction constant is therefore

$$F_0 = \zeta \sum_l \psi_l = \zeta N \int_0^1 \psi(x) dx = \zeta N \psi_0. \quad (\text{B.19})$$

Since λ is proportional to $N^{1/2}$, for high molecular weights we may neglect the unity in the right-hand member of EQUATION (B.18) and obtain the limiting

result

$$F_0/\eta_0 = (3/8)(6\pi^3)^{1/2} (bN^{1/2})h,$$

with

$$h = f^{1/2}/[2 - f + 2^{1/2}(f - 1)], \quad (\text{B.20})$$

which has been given in the text as EQUATIONS (5.3) and (5.4), and which reduces for $f = 1$ or 2 to the KR result for linear chains.

Incidentally, we note that the general result can also be expressed in the form

$$F_0 = N\zeta/[1 + (\zeta/6\pi\eta_0 N) \sum_{i \neq s} \sum_s \langle r_{is}^{-1} \rangle], \quad (\text{B.21})$$

which does not display any special properties of the cruciform molecules here treated. It may be hoped that this equation turns out to be true for branched polymers in general.

References

1. STAUDINGER, H. & K. FISCHER. 1940. J. prakt. Chem. **157**: 19.
2. SCHULZ, G. V. 1939. Z. physik. Chem. (B) **44**: 227.
3. WHEELER, O. L. 1953. Ann. N. Y. Acad. Sci. **57** (4): 360.
4. FOX, T. G & S. GRATCH. 1953. Ann. N. Y. Acad. Sci. **57** (4): 367.
5. ZIMM, B. H. 1953. Ann. N. Y. Acad. Sci. **57** (4): 332.
6. ZIMM, B. H. 1948. J. Chem. Phys. **16**: 1099.
7. KRAMERS, H. A. 1946. J. Chem. Phys. **14**: 415.
8. ZIMM, B. H. & W. H. STOCKMAYER. 1949. J. Chem. Phys. **17**: 1301.
9. THURMOND, C. D. & B. H. ZIMM. 1952. J. Polymer Sci. **5**: 477.
10. FLORY, P. J. 1949. J. Chem. Phys. **17**: 303.
11. ZIMM, B. H., W. H. STOCKMAYER, & M. FIXMAN. To be published.
12. YAMAMOTO, M. 1951. Busseiron-Kenkyu. **44**: 36; 1952. C. A. **46**:1844; GRIMLEY, T. B. 1953. J. Chem. Phys. **21**: 185.
13. FLORY, P. J. & W. J. KRIGBAUM. 1950. J. Chem. Phys. **18**: 1086.
14. DEBYE, P. & A. M. BUECHE. 1948. J. Chem. Phys. **16**: 573.
15. ISIHARA, A. 1950. J. Phys. Soc. Japan. **5**: 201.
16. DEBYE, P. & F. BUECHE. 1952. J. Chem. Phys. **20**: 1337.
17. STAVERMAN, A. J. 1950. Rec. trav. chim. **69**: 163.
18. TOMPA, H. 1952. Trans. Faraday Soc. **48**: 363.
19. DOTY, P., M. BROWNSTEIN, & W. SCHLENER. 1949. J. Phys. & Colloid Chem. **53**: 213.
20. ZIMM, B. H. 1946. J. Chem. Phys. **14**: 164.
21. BAKER, W. O. 1947. J. Am. Chem. Soc. **69**: 1125.
22. DEBYE, P. 1946. J. Chem. Phys. **14**: 636; also earlier theories of Huggins and Kuhn.
23. KUHN, W. & H. KUHN. 1943. Helv. Chim. Acta. **26**: 1394; 1948. J. Chem. Phys. **16**: 838.
24. KIRKWOOD, J. G. & J. RISEMAN. 1948. J. Chem. Phys. **16**: 565.
25. FLORY, P. J. 1949. J. Chem. Phys. **17**: 303; FLORY, P. J. & T. G. Fox. 1951. J. Am. Chem. Soc. **73**: 1904.
26. FOX, T. G. & L. MANDELKERN. 1953. J. Chem. Phys. **21**: 187; and earlier references given therein.
27. HOWARD, R. O. 1952. Ph.D. Thesis. M. I. T. Cambridge, Mass.
28. FLORY, P. J. & J. R. SCHAEFGEN. 1948. J. Am. Chem. Soc. **70**: 2709.
29. WEIL, L. L. 1945. Ph. D. Thesis. Columbia Univ. New York.
30. KUHN, W. & H. KUHN. 1947. Helv. Chim. Acta. **30**: 1233.
31. KIRKWOOD, J. G. 1949. Rec. trav. chim. **68**: 649.
32. CHANDRASEKHAR, S. 1943. Rev. Modern Phys. **15**: 1.

APPLICATION OF VISCOSITY METHODS TO THE STUDY OF BRANCHING IN POLYSACCHARIDES*

By M. Wales, P. A. Marshall, S. Rothman, and S. G. Weissberg

National Bureau of Standards, Washington, D. C.

The object of this paper is to present methods for quantitative evaluation of branching in polymers from intrinsic viscosity data. In a previous article,¹ measurements of intrinsic viscosity and molecular weight of B-512 dextran† hydrolyzates were performed under a variety of conditions of solvent and temperature.

Similar measurements on a dextran produced by another strain of *Leuconostoc* (NRRL culture B-742) will be presented here. The B-742 dextran differs from the B-512 dextran in that it is more highly branched. Structural parameters of the two dextrans will be presented and the results compared.

To summarize briefly the methods employed to analyze the data, one has from the Flory-Fox theory²

$$[\eta] = KM^{1/2}g^{3/2}\alpha^3 \quad (1)$$

for any chain polymer. Here K is a constant independent of solvent and molecular weight; α is an expansion factor which allows for the effect of the solvent and the volume effect on the volume pervaded by the segments of the chain; and g is the ratio of the squares of the unperturbed radii of gyration³ of branched and unbranched molecules having the same chemical constitution.

$$g = \frac{\bar{R}_0^2}{\bar{R}_{00}^2} \quad (2)$$

For linear molecules, $g = 1$. At the temperature $T = \theta$, where $\alpha = 1$, and the second virial coefficient is zero,

$$[\eta] = KM^{1/2}g^{3/2} \quad (3)$$

as M becomes small, g approaches 1. If we plot

$$\frac{[\eta]^{2/3}}{M^{1/2}} \text{ vs. } \frac{M}{[\eta]} \text{ at } T = \theta,$$

we obtain $K^{2/3}$ for an intercept at $M = 0$. For linear polymers, the slope of this curve is zero. For branched polymers, it is always negative. Then at any value of M ,

$$g = \frac{\frac{[\eta]^{2/3}}{M^{1/2}}}{\frac{K^{2/3}}{K^{1/3}}} = \frac{(\text{ordinate})}{(\text{intercept})} \quad (4)$$

Similar methods have been used in studying branched polystyrenes.⁴

* The authors are grateful to Florence R. McCann, Louis C. Williams, and D. R. Sears for assistance in some of the experimental work.

† Produced by *Leuconostoc Mesenteroides*, B-512 culture (Northern Regional Research Laboratory).

The θ temperature can be found by measuring the second virial coefficient⁴ as a function of temperature or by extrapolation of critical precipitation temperatures in a given solvent to infinite molecular weight, for a series of fractions.^{1, 2}

For the B-742 dextrans, the θ temperature was selected as 25°C and the composition of a methanol-water mixture which gave a zero second virial coefficient was found by light-scattering measurements (FIGURE 1). The three solid points on FIGURE 1 represent the addition of two successive amounts of water to a 49.4 per cent methanol solution of polymer. For practical purposes,

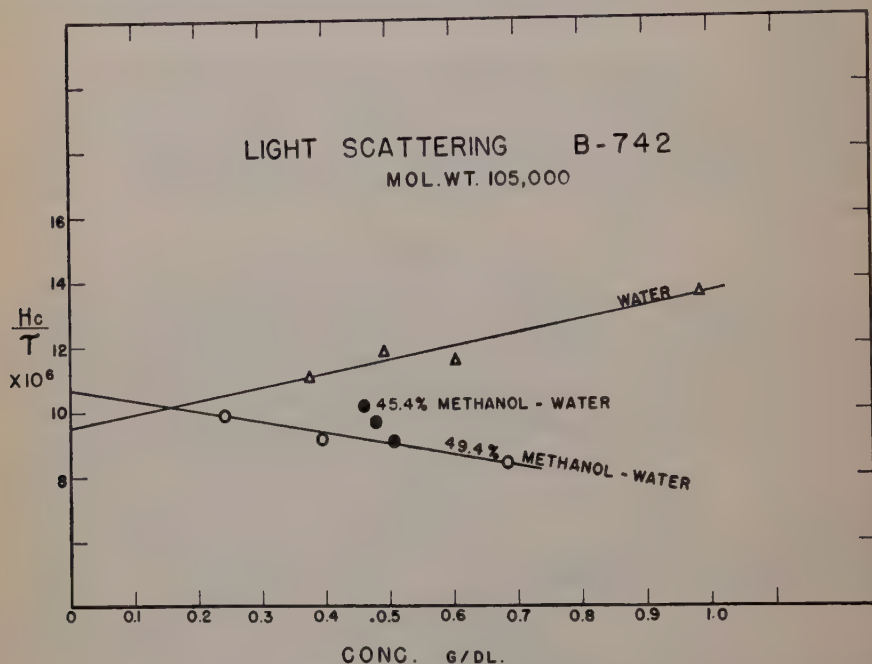


FIGURE 1. Determination of θ point.

methanol and water have refractive indices close enough together, so that no anomalies due to preferential adsorption would be expected.⁵ Note in TABLE 1 that the intrinsic viscosity is not sensitive to methanol concentration in the range 49–45 per cent by volume.

Data for B-512 and B-742 dextran hydrolyzates are given in FIGURE 2, where $\frac{[\eta]^{2/3}}{M^{1/3}}$ is plotted *versus* $\frac{M}{[\eta]}$. Intrinsic viscosity and molecular weight data for B-742 fractions are listed in TABLE 1. It can be seen that Flory's constant K is nearly the same for both dextrans, regardless of branching, since the intercepts in FIGURE 2 at $\frac{M}{[\eta]} = 0$ are nearly the same. The upward curvature for the B-742 curve in methanol solution is real since $[\eta]$ is practically independent

TABLE 1
 INTRINSIC VISCOSITIES AND MOLECULAR WEIGHTS FOR B-742 DEXTRANS*

Fraction	Intrinsic viscosity, 25°C			M_n^\dagger	M_w^\dagger	M_v^{**}	$A_2 \times 10^{4\dagger\dagger}$
	Water	49.4% CH ₃ OH	45.4% CH ₃ OH (θ composition)				
1.2	0.192	0.12	—	92,200	181,000	137,000	1.5
2.2	0.178	0.12	0.12	62,400	105,000	85,000	2.1
3.2	0.165	0.10	—	31,600	52,400	42,600	3.0
4.2	0.144	0.10	0.11	26,600	38,500	33,200	4.1

* The authors wish to thank Doctor F. R. Senti of the Northern Regional Research Laboratory, U. S. Department of Agriculture, for furnishing the native B-742 dextran from which our materials were prepared by acid hydrolysis and double fractionation from methanol-water mixtures, initial polymer concentration 1 per cent.

† By Somogyi copper reduction. Experiments performed by Mr. C. Snyder. (Report to the Office of the Surgeon General, Department of the Army; NBS Report 1713.)

‡ Light scattering measurements in water, dissymmetry ratio ca. 1.00. It is believed that the apparent wide molecular weight distribution of the fractions is real.

** From M_w and M_n assuming a logarithmic distribution of molecular weights and $[\eta] = KM^{0.18}$ in water.

†† Second virial coefficient from light scattering measurements, cgs units.

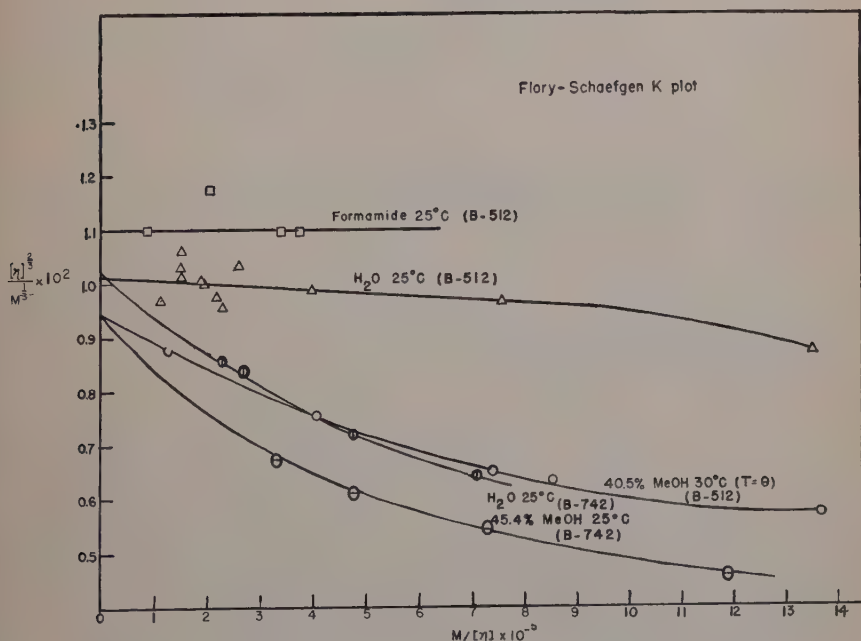


FIGURE 2. Viscosity behavior of B-512 and B-742 dextrans under various conditions.

of M (see TABLE 1). This is what would be expected of two polymers of the same chemical constitution, differing only in the arrangement of the monomer units.¹ The small differences in the intercepts at $\frac{M}{[\eta]} = 0$ may be the result of experimental error; or the value of the constant $\Phi^{2,4}$ may change slightly in going from one solvent to another.

Values of g may be obtained from the plot of FIGURE 2. These have been compared with values calculated from a Staudinger model¹ by Kramers's Theorem.⁶ This model has been assumed to have branches of uniform length,

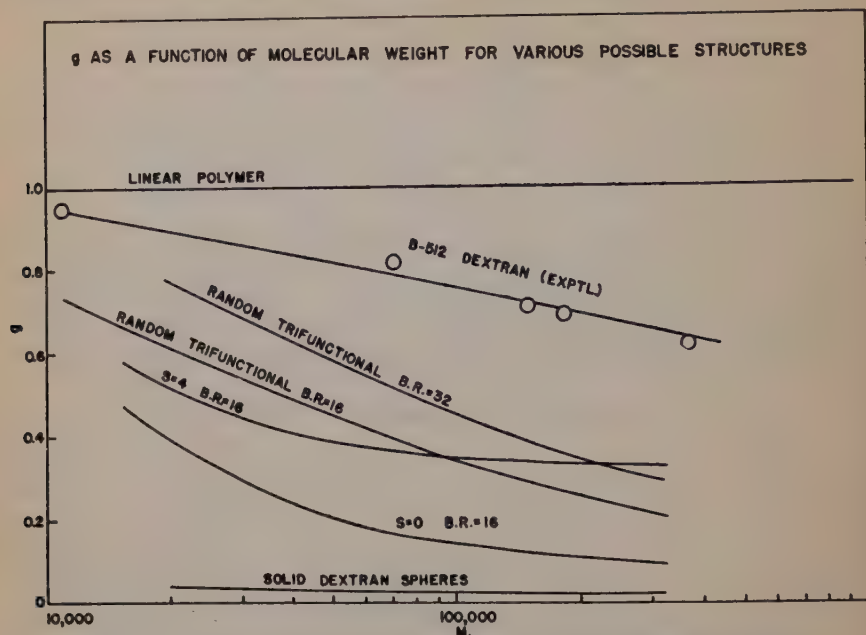


FIGURE 3. g as a function of molecular weight for various possible structures, B-512 dextran.

uniformly spaced on a main chain. We find for the g factor for this model,

$$g = \frac{6}{N^3} \left\{ \sum_{i=1}^{\epsilon_1} i(N-i) + \sum_{i=1}^{\epsilon_2} i(N-i) + k \sum_{i=1}^r i(N-i) + \sum_{P=1}^{P=k-1} \sum_{i=\epsilon_1+Pr+(P-1)S+P}^{i=\epsilon_1+Pr+Ps+P} i(N-i) \right\} \quad (5)$$

where r = branch length, S = number of glucose units between branches, and k = number of branches in a molecule of N units. A very wide variety of structures may be represented by proper choice of parameters (see FIGURE 3). Note that it would be difficult to distinguish between random trifunctional branching³ and the Staudinger model in one case, for $S = 4$, FIGURE 3. The values for the branching ratio or "B.R." given on the curves represent the ratio of 1,6 glucosidic linkages to non-1,6 glucosidic linkages for these materials. It has been assumed in the past^{7, 8, 9, 10} that the non-1,6 linkages in dextran are points of branching.

If this assumption is made, it can be seen that the B-512 and B-742 dextrans are not randomly branched (see FIGURE 4.). This is not an unreasonable result for a material of biological origin. In TABLE 2, branch lengths and spacings calculated from the model for B-742 and B-512 dextran are presented.

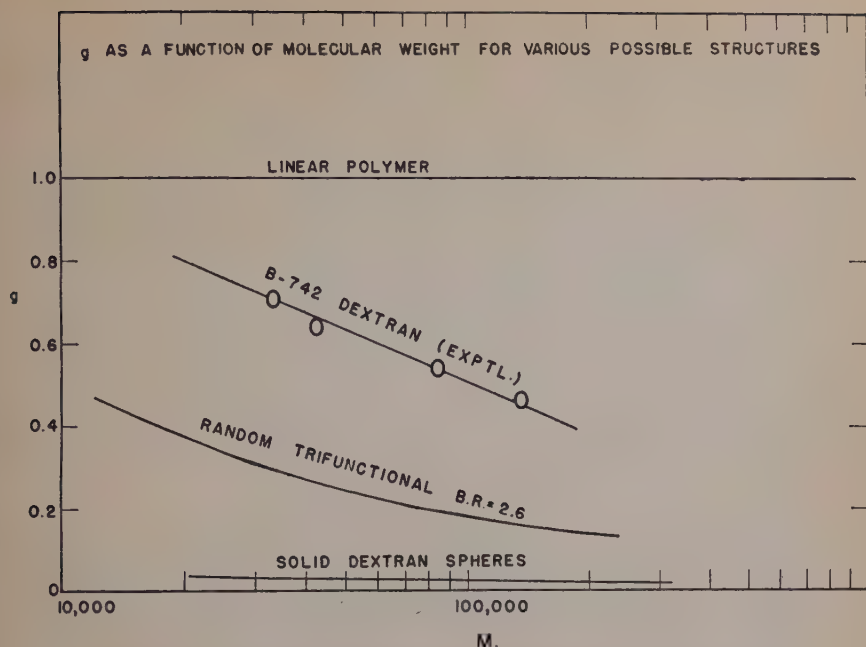


FIGURE 4. g as a function of molecular weight for various possible structures, B-742 dextran.

TABLE 2
CALCULATED AND EXPERIMENTAL g FACTORS FOR DIFFERENT DEGREES OF BRANCHING

Viscosity avg. mol. wt.	B-512 Dextran						
	Branching ratio 16*				Branching ratio 32		
	g exp.†	g calc'd	Branch length, glucose units	Spacing, glucose units	g calc'd	Branch length, glucose units	Spacing, glucose units
	M_v						
16,200	0.94	0.95	1	16	—	—	—
80,300	0.81	0.80	4	11	0.81	8	22
160,300	0.70	0.61, 0.80	5, 4	10, 11	0.70	10	21
324,000	0.62	0.63	6	9	0.63	12	19
	B-742 Dextran						
	Branching ratio 2.6‡						
	g exp.	g calc'd	Branch length, glucose units		Spacing, glucose units		
	M_v						
33,200	0.71	0.66	1.3		1.3		
42,600	0.65	0.62	1.4		1.2		
85,000	0.54	0.54	1.7		0.9		
137,000	0.46	0.42	2.1		0.5		

* Branching ratios for B-512 are difficult to measure; values previously found have been from 16 to 32. (H. S. Isbell, unpublished data; Commercial Solvents Corp., unpublished data).

† g values read from a plot of g vs. $\log M_v$.

‡ Report of Working Conference on Dextran, Northern Regional Research Laboratory, Peoria, Ill., July 9 1951.

Given g and the branching ratio, these quantities are fixed. The branch lengths found are of the same order of magnitude previously found for dextran by classical organic chemical methods.^{9, 10} The apparent difference between the two dextrans is that the B-742 has many more and shorter branches.

If it is assumed, however, that only a few of the non-1,6 linkages are branch points, and that all the materials are randomly branched, the g values observed for both the B-512 and B-742 dextrans are consistent with only 8 per cent of the non-1,6 linkages as branch points, in each case.

Having obtained g , we can calculate the swelling factor α^2 by which all linear

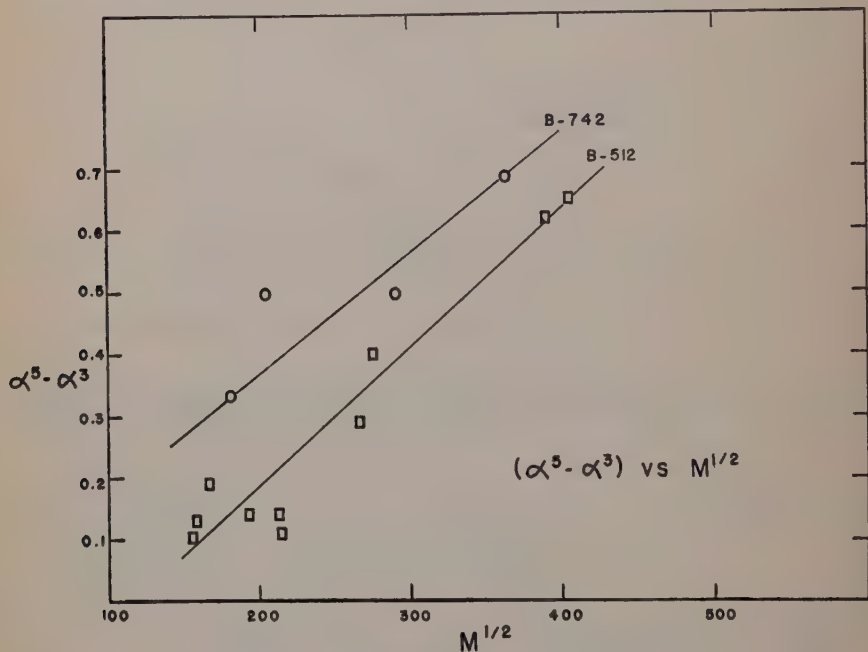


FIGURE 5. Swelling factors for B-512 and B-742 dextrans.

dimensions of the molecule are increased in going from a θ solvent to another solvent. The quantity $\alpha^5 - \alpha^3$ is plotted *versus* $M^{1/2}$ for B-512 and B-742 dextrans in water in FIGURE 5. The expansion of the more branched molecules is apparently higher, as would be expected from the larger volume effect to be found with a denser packing of segments.

So far we have indicated how quantitative information on branching can be obtained from studies of this kind. However, assumptions have been made. We have assumed that in θ solvents we have unperturbed molecular configurations and that Flory's picture of the behavior of the intrinsic viscosity is correct. There is a large amount of experimental evidence² to support the latter point of view. The fact that $[\eta] = KM^{1/2}$ for linear polymers in θ solvents is presumptive evidence for the correctness of our approach. Work which is

needed in order to check the validity of branching parameters obtained from viscosity data includes the following:

1. Studies of intrinsic viscosity *versus* molecular weight in several θ solvents for the same series of branched polymers, at the same temperature, to assess the real independence of g with respect to solvent.

2. Preparation and study of simple branched polymers of known constitution. This could be done by re-esterification of polyvinyl alcohol with acetic anhydride and subsequent ester interchange with long-chain fatty acids. A homologous series of branched polymers of fatty acid content independent of molecular weight, at least for sufficiently large molecular weights, should be obtained by this procedure.

3. Simultaneous measurement of θ by the precipitation temperature and virial coefficient methods, such as osmotic pressure, light scattering or the ultracentrifuge, to test the validity of this approach in mixed solvents.

References

1. WALES, M., P. A. MARSHALL, & S. G. WEISSBERG. 1953. *J. Polymer Sci.* **10**: 229.
2. FLORY, P. J. & T. G. FOX, JR. 1951. *J. Am. Chem. Soc.* **73**: 1904.
3. ZIMM, B. H. & W. H. STOCKMAYER. 1949. *J. Chem. Phys.* **17**: 1301.
4. THURMOND, C. D. & B. H. ZIMM. 1952. *J. Polymer Sci.* **5**: 477.
5. STOCKMAYER, W. H. 1950. *J. Chem. Phys.* **18**: 58; KIRKWOOD, J. G. & R. J. GOLDBERG. 1950. *J. Chem. Phys.* **18**: 54.
6. KRAMERS, H. A. 1946. *J. Chem. Phys.* **14**: 415.
7. PEAT, S., E. SCHLUCHTERER, & M. STACEY. 1939. *J. Chem. Soc.* : 581.
8. HASSID, W. Z. & H. A. BARKER. 1940. *J. Biol. Chem.* **134**: 163.
9. LEVI, I., W. L. HAWKINS, & H. HIBBERT. 1942. *J. Am. Chem. Soc.* **64**: 1959.
10. STACEY, M. & G. SWIFT. 1948. *J. Chem. Soc.* : 1555.

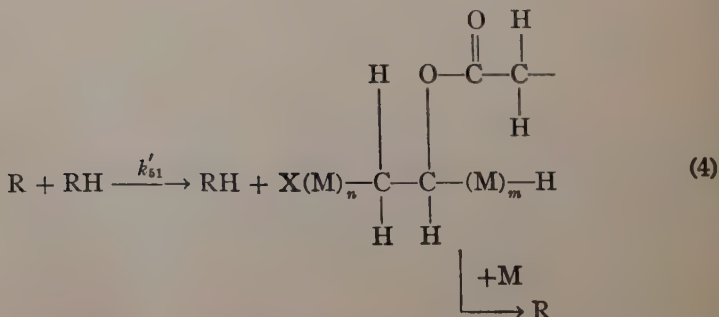
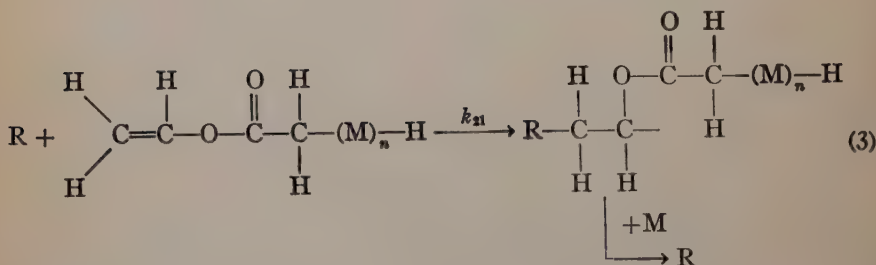
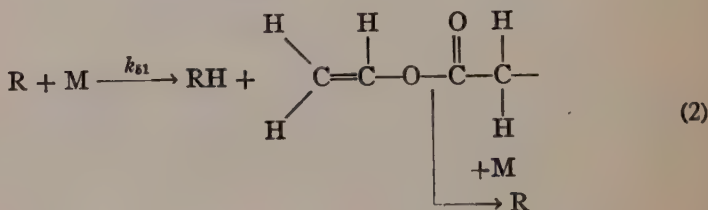
RELATION BETWEEN DEGREE OF BRANCHING AND DEGREE OF CONVERSION DURING POLYMERIZATION

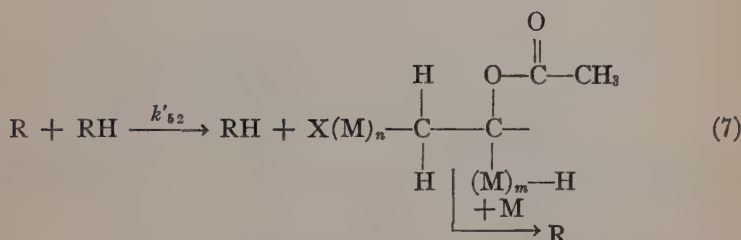
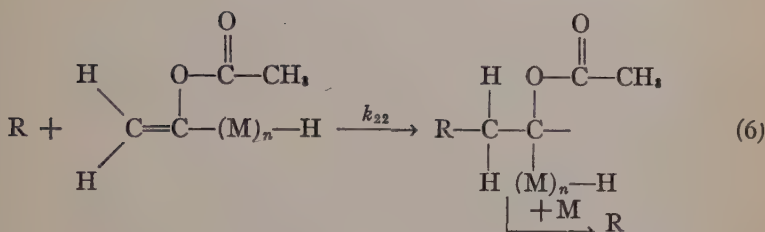
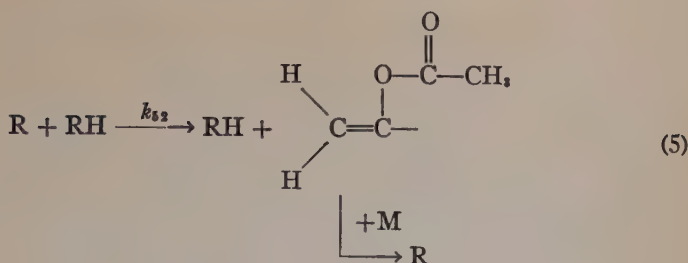
By O. L. Wheeler

Colton Chemical Company, Cleveland, Ohio

It is now well known that, during the free radical, addition polymerization of vinyl type monomers, transfer with the monomer and polymer may occur. With these considerations in mind, it requires only a simple extension of current theories of transfer and copolymerization to develop a mechanism for the formation of polymer branches.

This mechanism is illustrated in reactions (1) through (7) in the case of vinyl acetate. This monomer is particularly suitable for study not only because the chemical nature of some of the branches makes their quantitative measurement relatively simple but also because the monomer contains two active transfer bonds that have been shown to differ greatly in their properties.^{1, 2}





R is a polymer radical, RH is a polymer molecule, M is a monomer molecule, X is an initiating radical, and the k's are reaction rate constants.

These equations represent reactions with seven different chemical bonds and the production of seven different free radicals. Since each of these radicals could react with each of the chemical bonds, a mathematically unmanageable system exists. This has been simplified by assuming that all radicals quickly add to the monomer double bond to form the normal polymer radical so that the concentrations of all but this radical may be neglected. Some justification for this assumption is based on the reasoning that if a radical did exist that added only slowly to the monomer, only very low molecular weight polymers could be obtained. While this does not apply to vinyl acetate, it may apply to other monomers.

Further simplification is obtained by considering polymerization systems containing only pure monomer and a negligible concentration of initiator. Under these conditions, the influence of initiator radicals and possible transfer agents can be neglected and the molecular weight of the polymer, as well as the degree of branching, is governed solely by the seven listed reactions. Mathematically, the maximum molecular weight and the degree of branching at every degree of conversion can be related to six ratios of the seven reaction

rate constants. In calculating the maximum molecular weight of the branched polymer molecules when two or more transfer bonds exist in the monomer, non-integrable expressions are obtained. These can be avoided if it is assumed that the several transfer reactions influence the molecular weight independently of each other. This assumption is not necessary if a purely arithmetical solution is required.

The number average degree of polymerization of the branched molecules, \bar{P}_{nb} , is given by EQUATION (8).

$$\bar{P}_{nb} = ([M_0] - [M]) / ([P_1] + [P_2]) \quad (8)$$

in which $[M_0]$ represents the initial and $[M]$ the final concentration of monomer, and $[P_1]$ and $[P_2]$ represent the concentrations of polymer molecules having hydrolyzable and non-hydrolyzable double-bond end groups respectively. By hypothesis these are the only types of polymer molecules present and can be calculated by EQUATIONS (9) and (10).

$$[P_1] = \left[\frac{k_{51}/k_2}{(1 - k_{21}/k_2)} \right] \left[\frac{[M_0]^{(1-k_{21}/k_2)} - [M]^{(1-k_{21}/k_2)}}{[M]^{-k_{21}/k_2}} \right], \quad k_{21} \neq k_2 \quad (9a)$$

$$[P_1] = (k_{51}/k_2) [M] \ln ([M_0]/[M]), \quad k_{21} = k_2 \quad (9b)$$

$$[P_2] = \left[\frac{k_{52}/k_2}{(1 - k_{22}/k_2)} \right] \left[\frac{[M_0]^{(1-k_{22}/k_2)} - [M]^{(1-k_{22}/k_2)}}{[M]^{-k_{22}/k_2}} \right], \quad k_{22} \neq k_2 \quad (10a)$$

$$[P_2] = (k_{52}/k_2) [M] \ln ([M_0]/[M]), \quad k_{22} = k_2 \quad (10b)$$

The number average degree of polymerization of the straight chain segments, \bar{P}_{ns} , is given by EQUATION (11).

$$\bar{P}_{ns} = \frac{k_2}{(k_{51} + k_{52}) + (k'_{51} + k'_{52})} \left[\left(\frac{[M_0]}{[M_0] - [M]} \right) \left(\ln \frac{[M_0]}{[M]} \right) - 1 \right] \quad (11)$$

The number average degree of polymerization of the polymer after hydrolysis, \bar{P}_{nh} , is given by EQUATION (12) in which P_{s1} can be calculated by EQUATION (13).

$$\bar{P}_{nh} = ([M_0] - [M]) / ([P_2] + [P_{s1}]) \quad (12)$$

$$[P_{s1}] = ([M_0] - [M]) \left[\frac{k_{51} - k'_{51}}{k_2} \right] + \left(\frac{k'_{51}}{k_2} \right) [M_0] \ln \frac{[M_0]}{[M]} \quad (13)$$

The degree of branching of the original and hydrolyzed resins, \bar{B}_b and \bar{B}_h respectively, are:

$$\bar{B}_b = (\bar{P}_{nb}/\bar{P}_{ns}) - 1 \quad (14a)$$

$$\bar{B}_h = (\bar{P}_{nh}/\bar{P}_{ns}) - 1 \quad (14b)$$

In FIGURE 1, curves A, B, and D pertain to monomers containing only a single transfer bond. They show the variation in maximum molecular weight

with conversion, relative to its value at zero conversion, for differing reactivities of the double-bond end group. The numbers in parentheses are the numerical values of the ratio, k_{21}/k_2 . Curve C is typical of a monomer containing two transfer bonds for which the ratios k_{21}/k_2 and k_{22}/k_2 are unity and zero respectively. It illustrates the fact that whenever a non-reactive double-bond end group is produced, there is a maximum molecular weight at even very high conversions. Curves D, E, and F represent the variation in molecular weight of the straight chain segments with conversion for several values of k'_{51}/k_{51} . The shape of the curves is not altered by a multiplicity of transfer bonds.

The experimental approach involved the preparation of highly purified vinyl acetate and placing it in sealed Pyrex tubes. The tubes were then placed in a

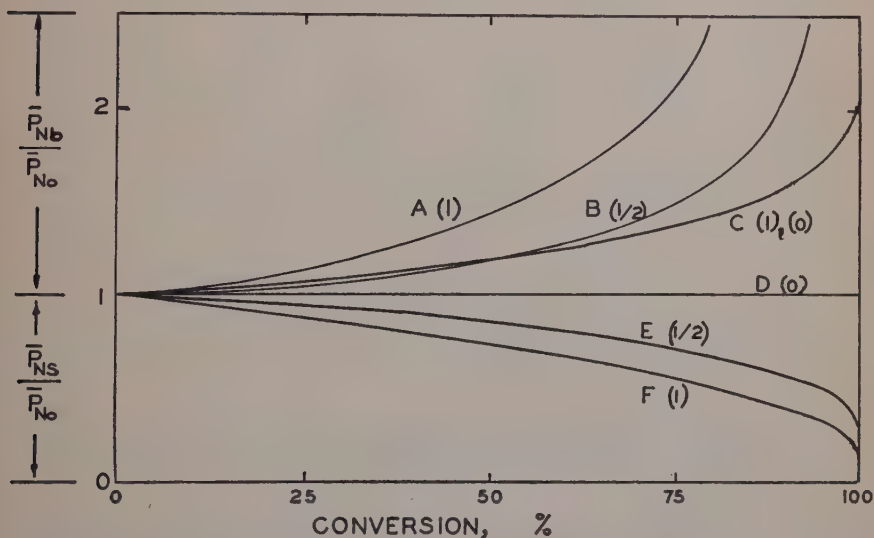


FIGURE 1. Calculated variation in maximum degree of polymerization of branched molecules and straight segments with conversion for several values of the rate constant ratios.

constant temperature bath and irradiated with very weak ultraviolet light. At the desired conversion, as estimated from the decrease in volume, the tubes were removed and cooled, the conversions accurately measured, and the polymer recovered.

The molecular weights of these polymers were estimated by both intrinsic viscosity measurements and analyses of double-bond end groups. These measurements were in good agreement with the viscosity and osmotic measurements of Wagner.³ The results on two series of these polymers prepared at 70°C are shown in FIGURE 2. The solid line of the upper curve was calculated with four rate-constant ratios selected by trial and error. The assignment of numerical values to these ratios was greatly aided by a few significant characteristics of the curve. Since the molecular weight of the polymer tends toward a maximum at even very high conversions, there must be at least one type of double-bond end group that polymerizes very slowly or not at all. This led to the conclu-

sion that $k_{22}/k_2 = 0.0$. The maximum number average degree of polymerization at zero conversion was approximately 3000. This meant that the sum of the reciprocals of k_2/k_{51} and k_2/k_{52} would equal the reciprocal of 3000. The best values were found to be: $k_{22}/k_2 = 0.0$, $k_{21}/k_2 = 1.0$, $k_2/k_{52} = 11,000$ and $k_2/k_{51} = 4125$.

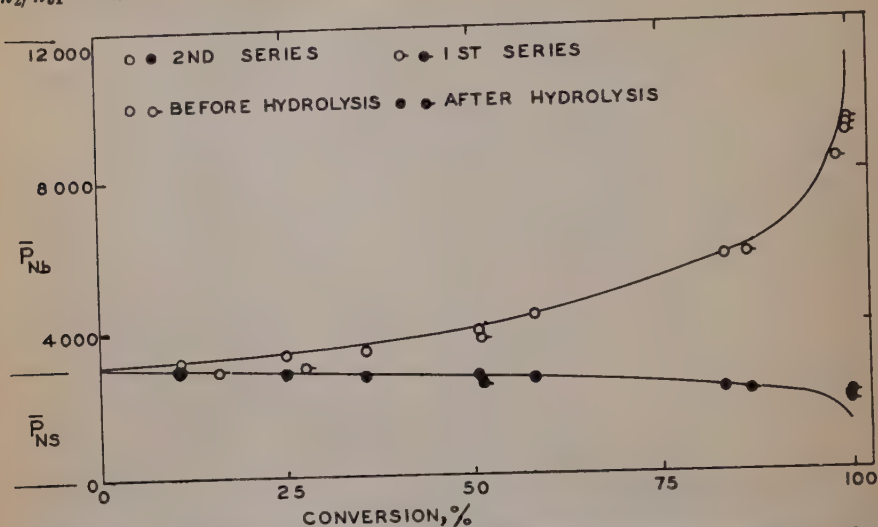


FIGURE 2. Experimental values for the maximum degree of polymerization of vinyl acetate at 70°C before and after hydrolysis.

TABLE 1
MONOMER UNITS PER DOUBLE BOND BEFORE AND AFTER HYDROLYSIS

Conversion	Monomer units	
	Before	After
<i>Per cent</i>		
10.9	3,060	9,700
25.3	3,060	11,600
35.8	3,200	9,700
50.9	4,150	8,900
58.1	4,150	5,300
83.4	6,900	5,800

At this point, it may seem arbitrary to assign the zero value to k_{22}/k_2 rather than k_{21}/k_2 . The double-bond end group, however, resulting from transfer with the acetate group resembles an exceedingly high molecular weight vinyl ester. Port, Jordon, Hansen and Swern⁴ have shown that the monomer reactivity ratios for the copolymerization of vinyl acetate and vinyl palmitate are quite close to unity. More direct experimental evidence is based on the fact that type one double-bond end groups would be destroyed upon hydrolysis or saponification of the polymer. In TABLE 1 are listed double-bond end group measurements on some of the polymers before and after hydrolysis and acetyla-

tion. The latter measurements should all approximate 11,000. Since the unsaturation of one of the polymers increased on processing, there is apparently some method by which double bonds can be formed during the treatment. This may possibly occur through dehydration of polyvinyl alcohol. Half of the measurements, however, were of the expected order of magnitude.

TABLE 2
MONOMER UNITS PER BRANCH, TOTAL AND HYDROLYZABLE

Conversion	Batch process		Continuous process	
	Hydrolyzable	Total	Hydrolyzable	Total
<i>Per cent</i>				
0	∞	∞	∞	∞
20	22,000	12,500	15,000	9,200
40	12,000	6,700	4,750	3,150
60	6,400	3,700	2,550	1,550
80	4,300	2,000	1,200	650
90	3,400	1,450	600	300
95	2,800	1,100	300	150
99	2,200	690	60	30

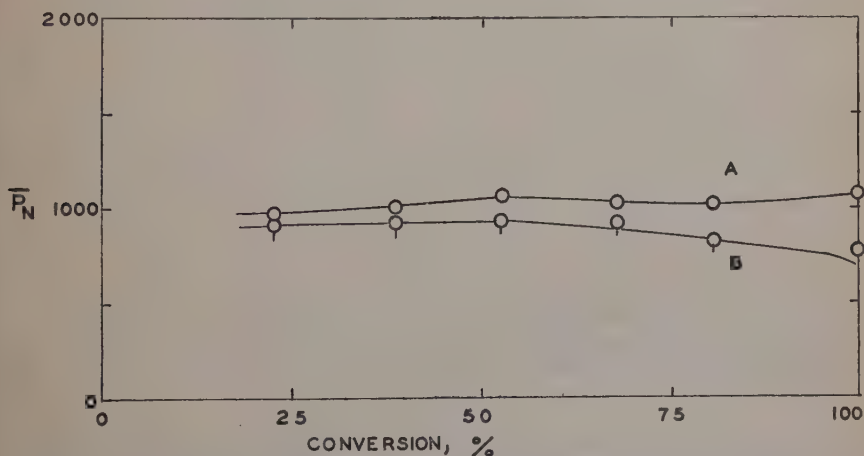


FIGURE 3. Calculated and observed change in degree of polymerization upon hydrolysis of vinyl acetate polymers prepared in benzene at 70°C.

The branches formed as the result of reactions (2) and (4) will be broken from the stems on hydrolysis of the polymer. Measurement of the molecular weight of the polymer after hydrolysis provides a means of estimating the value of k'_{51}/k_{51} . Viscosity measurements on polyvinyl alcohol, however, are not reliable so that the polymers were acetylated after hydrolysis and measurements made on the reformed polyvinyl acetate. Results are shown in the lower curve of FIGURE 2. The solid curve is calculated on the basis that $k'_{51}/k_{51} = 0.4$. This low value was taken in an unsuccessful attempt to obtain a curve that would fit the data at high conversions. The failure to obtain a

curve of the expected shape may indicate that our original assumptions are decreasingly valid at high conversions. Another possibility is that some of the ester linkages are reformed during acetylation. If this does occur, it would be most pronounced at high conversions.

By a method involving crosslinking of the polymer, Wheeler, Lavin and Crozier² obtained an approximate value of 0.5 for k'_{51}/k'_{52} . Stockmayer⁵ and his coworkers, however, succeeded in obtaining a direct measurement of the transfer constant of polyvinyl acetate and found that it was about three times the transfer constant of the monomer. If $k'_{51}/k_{51} = 1.0$, then k'_{51}/k'_{52} would be approximately 0.33. More accurate experimental evidence, particularly in the region of high conversion, is required to provide reliable values for these ratios.

On the basis of their values for the rate constant ratios Wheeler, Lavin and Crozier² calculated the number of monomer units per branch, both total and hydrolyzable, as a function of conversion. These calculations included both the normal batch process and the "single kettle continuous" process. The latter process is concerned with a vigorously agitated kettle, held at constant temperature, and into which the reactants are fed and from which the products are removed at a constant rate. These calculations are shown in TABLE 2. They used these data to calculate the degradation on hydrolysis of a series of polymers prepared in benzene at 70°C with benzoyl peroxide and commercial grade monomer. The results are shown in FIGURE 3. All points and curve A were experimentally determined. Curve B was calculated and is in good agreement with the experimental results.

Despite the success of the foregoing experiment, caution must be used in making such calculations on polymerization systems in which the probability of crosslinking is large.

References

1. WHEELER, O. L., S. L. ERNST, & R. N. CROZIER. 1952. J. Polymer Sci. **8**: 409.
2. WHEELER, O. L., E. LAVIN, & R. N. CROZIER. 1952. J. Polymer Sci. **9**: 157.
3. WAGNER, R. H. 1947. J. Polymer Sci. **2**: 21.
4. PORT, W. S., E. F. JORDAN, JR., J. E. HANSEN, & D. SWERN. 1952. J. Polymer Sci. **9**: 493.
5. STOCKMAYER, W. H. Private Communication.

CROSSLINKING IN MONOVINYL MONOMERS

(I). BY CHAIN TRANSFER WITH THE POLYMER CHAIN

By T. G. Fox and Serge Gratch

Rohm and Haas Company, Philadelphia, Pa.

Introduction

It is known that certain monovinyl monomers, notably methyl acrylate and vinyl acetate, form crosslinked insoluble network polymers on bulk polymerization in the absence of chain transfer agents. For methyl acrylate, macrogelation may occur at conversions (α) below 5 per cent,^{1, 2, 3} and microgelation, resulting in a heterogeneous polymerization to an insoluble popcorn type of polymer, has been observed in thermal polymerizations at conversions appreciably less than 1 per cent.^{3, 4} In the polymerization of vinyl acetate gelation has been observed at very high conversion.⁵ Gelation is not observed in the bulk homopolymerization of other common monomers such as styrene or methyl methacrylate.

It has been demonstrated recently that branching occurs in vinyl acetate as the result of chain transfer reactions with the monomer and with the polymer chains.⁶ It has long been suspected² that, in methyl acrylate, chain transfer with the "active" alpha hydrogen atom on the carbon adjacent to the carbonyl carbon atom will occur and thereby lead to branching. Recent studies of the chain transfer constants with methyl acrylate of methyl 2-ethyl butyrate and of methyl isobutyrate, bear this out.⁷ The very high molecular weights obtained even at low conversions in the polymerization of methyl acrylate,^{1, 3} on the other hand, indicate that branching *via* chain transfer with the monomer is unimportant in this case. Since crosslinking results if two branch radicals combine, and since a particular molecule may contain more than one branch, it will be recognized that, under certain conditions, a mechanism involving branching and termination by combination can lead to gelation.

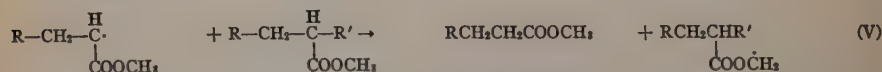
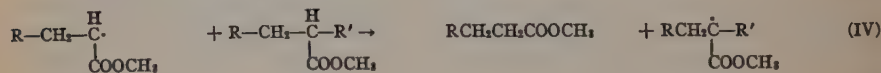
It is the purpose of this paper to consider the possibility of gelation in the particular case wherein branching occurs solely by chain transfer with the polymer chain. Predictions concerning the gel point (if any) are made in terms of the number of active transfer sites per chain (n_B), and the relative probability that the growth of a radical will be interrupted by combination with another radical rather than by chain transfer. The simple case of the graft copolymerization of a monomer with a polymer containing the same number of active transfer sites on each molecule is treated rigorously. An approximate treatment concerning gelation in the homopolymerization of monovinyl monomers yields results which are at least qualitatively in accord with the observations mentioned heretofore. This preliminary treatment is sufficiently precise to reveal why the tendency to gelation decreases in the order: methyl acrylate > vinyl acetate \gg styrene > methyl methacrylate. Methods are suggested for treating more exactly the conditions leading to macrogelation, or microgelation and inhomogeneous polymerization. These will be developed in future publications.

General Considerations

Wherever a branch radical combines with another branch radical, it forms a crosslink between the two macromolecules involved. Wherever the number of crosslinks thus formed exceeds a certain critical fraction of the number of chains, usually taken as $\frac{1}{2}$,⁸ an infinite molecular weight crosslinked insoluble network may result. It will be shown that the attainment of an infinite network is dependent on the relative rates of various competitive reactions. In order to keep the mathematical complications within bounds, the analysis will be carried out for special cases in which only a small number of kinetically different reactions need be considered. An attempt will be made to indicate what modifications of the analysis are needed in other cases.

In the case of graft copolymerization by a chain transfer mechanism, the appropriate simplifying assumptions are rather obvious. For practical reasons graft copolymerization of this type usually is of interest only when the chain transfer constant of the active sites on the parent polymer is so high that all other branching mechanisms in the system are of negligible importance. It may be necessary, however, to consider monomer transfer and chain transfer to a solvent added for the express purpose of limiting the size of the branches, but only in so far as these limit the lifetime of the branch radicals.

The situation is more complicated in homopolymerization, since several sources of branches may be equally important. Thus, transfer reactions with the monomer or with the polymer may occur by several mechanisms, illustrated below for methyl acrylate:



Other less likely transfer reactions are not shown. The last two reactions lead to branching if the radicals involved propagate, whereas, in the first two cases, branching follows only if, subsequent to the propagation of the resulting free radicals, a chain grows through the remaining double bond. The third reaction generally would not be expected to lead to branching, since the double bond produced should be quite inert in free radical polymerization.

In methyl acrylate, reactions (II) and (V) cannot be important sources of branching in view of the complete insolubility of the hydrolyzed crosslinked homopolymer.³ The chain transfer constant for (I) at 60° is estimated, from the high intrinsic viscosity ($[\eta] \sim 6$) of the extractable portion of the pre-

dominantly crosslinked, thermally polymerized, methyl acrylate,³ to be not appreciably greater than 10^{-5} , whereas the transfer constant for (IV) at this temperature may be estimated from Flory's data⁷ to be greater than 10^{-4} . Thus, in methyl acrylate, reaction (IV) is the chief source of branching. This, however, is not necessarily the case for other monomers. For vinyl acetate reactions analogous to (I), (II), (IV), and (V) are all important sources of branching.⁶ In polyethylene, a reaction of type (III) may be an important source of branching, since it produces a vinyl group on a polymer chain, and may proceed at a significant rate at the relatively high temperature encountered in the polymerization of ethylene.⁹ For styrene, estimated chain transfer constants (see TABLE 4) for reactions (I) and (IV) are not too dissimilar, indicating that both may be important sources of branching. For methyl methacrylate, which contains no hydrogen atoms in the alpha position, these constants are very low, indicating that branching is relatively infrequent in this case.

While any of the above reactions may be important sources of branching, it appears that, for many vinyl monomers, reaction (IV) involving the transfer of the reactive alpha hydrogen on the polymer chain, will be the main source of branching. In the analysis of branching and gelation in homopolymerization presented here, therefore, reactions of this type will be considered to be the *only* source of branching. The results will be strictly applicable only in cases analogous to that of methyl acrylate. For vinyl acetate, in particular, the present results must be considered very approximate. The treatment required for cases wherein reaction (IV) is not the chief source of branching is an obvious generalization of the present work.

Graft Copolymerization

A copolymer containing long sequences of different chemical units has been termed a *graft* copolymer.¹⁰ One method for the preparation of a graft copolymer is to polymerize a monomer C in the presence of a backbone polymer of different composition. Chain transfer between the free radicals of C and labile atoms of the dissolved polymer will produce radicals whose subsequent growth forms branches composed of C units on the backbone chain. An early example of this type of copolymerization was reported by Carlin and Shakespeare¹¹ who polymerized p-chlorostyrene in the presence of a homopolymer (polymethyl acrylate) possessing one potential transfer site for each structural unit. A variation of this method which offers greater versatility and higher efficiency was explored recently by Alfrey and Bandel.¹² It involves the use of a copolymer as the backbone chain, wherein only a fraction of the structural units in the chain possess relatively labile atoms (*e.g.*, vinyl acetate polymerized in the presence of a copolymer of styrene and vinylidene chloride).

Although generally not enough data are available to indicate with certainty whether crosslinking occurred in the preparation of the graft copolymers which have been reported in the literature, it is obvious that this possibility must be considered. Actually, the treatment of this case is most simple, since the number of backbone chains to be crosslinked is fixed, and since the number of active transfer sites does not increase with increasing conversions, but rather

decreases in a predictable fashion. We shall choose, for purpose of illustration, conditions wherein an appreciable fraction of the polymer which forms will be present on the branches, a condition which is likely to obtain in any practical graft copolymerization.

Consider the graft copolymerization of a system containing initially parent polymer in concentration N_A and monomer in concentration C_0 . Each chain of parent polymer contains initially n_B chain transfer sites, so that the total initial concentration of these is $B_0 = n_B N_A$. The concentration of monomer at any time t is $C = (1 - \alpha_C)C_0$. The concentration of chain transfer sites at any time is $B = (1 - \alpha_B)B_0$. The concentration of free radicals not attached to the parent polymer is R_c . The concentration of branch radicals is R_B .

The reactions here considered are shown in TABLE 1, with the corresponding

TABLE 1
REACTIONS IN GRAFT COPOLYMERIZATION

No.	Reaction	Type	Rate
(VI)	$C \rightarrow R_c$	Initiation	$2 k_i$
(VII)	$R_c + C \xrightarrow{k_p} R_c$	Propagation	$k_p C R_c$
(VIII)	$R_B + C \xrightarrow{k_p} R_B$	"	$k_p C R_B$
(IX)	$R_c + B \xrightarrow{k_B} R_c H + R_B$	Transfer	$k_B B R_c$
(X)	$R_B + B \xrightarrow{k_B} R_B H + R_B$	"	$k_B B R_B$
(XI)	$R_c + C \xrightarrow{k_m} R_c H + R_c$	"	$k_m C R_c$
(XII)	$R_B + C \xrightarrow{k_m} R_B H + R_c$	"	$k_m C R_B$
(XIII)	$R_c + S \xrightarrow{k_s} R_c H + R_c$	"	$k_s S R_c$
(XIV)	$R_B + S \xrightarrow{k_s} R_B H + R_c$	"	$k_s S R_B$
(XV)	$R_B + R_B \xrightarrow{k_t} R_B - R_B$	Termination	$k_t R_B^2$
(XVI)	$R_c + R_c \xrightarrow{k_t} R_c - R_c$	"	$k_t R_c^2$
(XVII)	$R_B + R_c \xrightarrow{2k_t} R_B - R_c$	"	$2 k_t R_B \cdot R_c$

rates. The initiation mechanism is immaterial for the present purpose, and therefore its rate is taken to be simply $2k_i$. For efficient graft copolymerization, the propagation rate of the free radicals produced at the first step of branching must not be too low, since otherwise the polymerization would be severely retarded. It follows that all but a negligible fraction of the free radicals present at any time on the ends of growing branches must be identical in structure with the radicals on the ends of other growing chains. The reactivities of all free radicals are assumed, therefore, to be the same. We shall assume, for purposes of generalization, that a chain transfer agent may be present in concentration S . Reaction with this agent is assumed to produce, with rate constant k_s , free radicals which propagate rapidly enough to have the same end groups as the other free radicals for most of their lives. The termination steps are considered to proceed exclusively by combination of two free radicals.^{13*} The rate constant $2k_t$ for the reaction (XVII) is consistent

* The generalization to the case in which a fraction of the free radicals terminate by disproportionation is obvious.

with the rate constants k_t for reactions (XV) and (XVI), as long as all free radicals have the same reactivities.

It is easily shown that the steady state assumption is applicable separately to the two kinds of free radicals here considered as soon as the two following conditions are satisfied simultaneously:

$$\alpha_c \gg (k_p/4k_t) \text{ and } \alpha_o \gg (k_p/2k_t) \left[1 + \frac{k_m C + k_s S + k_B B}{2k_t \sqrt{k_1/k_t}} \right]^{-1}.$$

These two conditions are satisfied in the range of conversions of practical interest for most of the monomers of interest.

With the steady state assumptions, the rates shown in TABLE 1 yield the following results:

$$R_e \cdot + R_B \cdot = \sqrt{k_i/k_t} = R_0 \cdot \text{ (a constant)} \quad (1)$$

$$R_B \cdot = \frac{(1 - \alpha_B)}{(1 - \alpha_B + y_0)} R_0 \cdot \quad (2)$$

where:

$$y_0 = \frac{2k_t R_0 \cdot + k_m C + k_s S}{k_B B_0} \quad (3)$$

The constant $R_0 \cdot$ is equal to the steady state concentration of free radicals which would obtain if no chain transfer with the polymer would take place. The parameter y_0 is the *initial* ratio of the probability that a free radical be terminated by combination with another free radical or by transfer to monomer or solvent, to the probability that it chain transfers with an active site on the backbone polymer.

The rate of formation of crosslinks X by reaction (XV) is:

$$\frac{dX}{dt} = k_t R_B^2 \cdot = \frac{k_t R_0^2 (1 - \alpha_B)^2}{(1 - \alpha_B + y_0)^2} \quad (4)$$

Time may be eliminated conveniently by the relation

$$\frac{d\alpha_B}{dt} = k_B R_0 \cdot (1 - \alpha_B) \quad (5)$$

Dividing EQUATION (4) by EQUATION (5):

$$\frac{dX}{d\alpha_B} = \frac{k_t R_0 \cdot}{k_B} \frac{(1 - \alpha_B)}{(1 - \alpha_B + y_0)^2} \quad (6)$$

A further simplification may be made when the terms $k_m C$ and $k_s S$ are negligible by comparison with $2k_t R_0 \cdot$. In this case,

$$y_0 \cong y'_0 = \frac{2k_t R_0 \cdot}{k_B B_0} \quad (3a)$$

and EQUATION (6) becomes

$$\frac{dX}{d\alpha_B} = \frac{1}{2} B_0 y_0' \frac{(1 - \alpha_B)}{(1 - \alpha_B + y_0')^2} \quad (7)$$

Integrating:

$$X = B_0 Z/2 \quad (8)$$

where

$$Z = y_0' \log_e [(y_0' + 1)/(y_0' + 1 - \alpha_B)] - \alpha_B y_0'^2 / (y_0' + 1)(y_0' + 1 - \alpha_B) \quad (9)$$

The condition for the formation of a crosslinked network (gelation) has been shown⁸ to be that the number of crosslinks equal or exceed half the number of primary chains, that is:

$$X/N_A \geq 1/2 \quad (10)$$

or, since $N_A = B_0/n_B$, by EQUATION (8):

$$n_B \geq (1/Z) \quad (11)$$

The criterion of EQUATION (11) for gelation to occur by the time a fraction α_B of B groups have formed branches is that the initial number of transfer sites on a backbone chain must exceed a critical value $(1/Z)$ which is a function of α_B and of y_0' , *i.e.*, of the fraction of sites which have been activated and the initial probability that a branch radical undergoes combination rather than transfer. Plots of $(1/Z)$ versus y_0' on logarithmic coordinates for various values of α_B (FIGURE 1) together with EQUATION (11) lead to two conclusions: (1) gelation will occur at lower and lower values of n_B the higher α_B is; and (2) for each α_B the value of n_B required for gelation goes through a minimum at some value of y_0' . The first relationship follows from the fact that at higher α_B 's more crosslinks are present, hence a greater number of chains can be tied together. The second is reasonable also on physical grounds, since if $k_B = 0$ (high y_0') no branching would occur, while for $k_B = \infty$ or $k_t = 0$ (low y_0') all of the sites form branches without any coupling taking place. In either extreme case, gelation could not occur even for infinite values of n_B . Necessarily then, the value of n_B required for gelation must go through a minimum for some value of y_0' between these two extremes. For $\alpha_B = 1$, the minimum of $(1/Z)$ is approximately 4.6, for y_0' approximately 0.46, *i.e.*, gelation is impossible if the number n_B of chain transfer sites on the backbone chain is four or less. It would be expected that this number must be greater than 1 since the mechanism of crosslinking assumed requires that both chain transfer and coupling be possible reactions and, accordingly, only a fraction of the branching sites is effective in forming crosslinks. It is impossible to guess what this fraction should be. A maximum value somewhere between $1/3$ and $1/4$, however, does not seem unreasonable, and it may be expected to occur when combination and transfer are equally probable, *i.e.*, at $y_0' \cong 0.5$. The decrease in this fraction at higher and lower values of y_0' means that a larger portion of the branch radicals is

terminated by transfer, or by combination with unattached $R_c\cdot$ radicals, respectively.

In choosing conditions for graft copolymerization which may be of practical interest, it seems desirable to have the efficiency of graft copolymerization (ϵ), defined as the fraction of the polymerized C units which are attached to the backbone chain, as high as possible without gelation. According to FIGURE 1 gelation is possible in principle only for values of y_0' in ranges determined by the curve for $\alpha_B = 1$. It would appear that gelation is least likely at either very high or very low values of y_0' . It is easily shown, however, that the

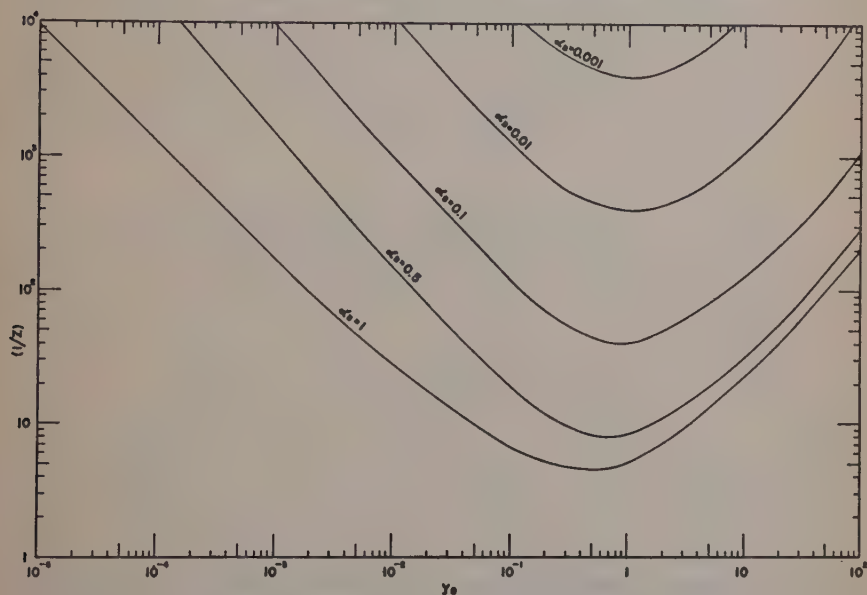


FIGURE 1. Gelation parameters in graft copolymerization.

initial value of the grafting efficiency is given by

$$\epsilon_0 = \frac{2}{2 + y_0'} \quad (12)$$

Therefore, to achieve a high efficiency, it is desirable to have y_0' as low as possible, say $y_0' \leq 0.1$ where $\epsilon_0 \geq 0.95$. Hence, to achieve high efficiency without gelation, it is generally desirable to have values of y_0' as low as practicable.

In order to obtain an equation suitable for the numerical calculation of y_0' in cases of practical interest, we shall make use of the following relationships:

$$d\alpha_c/dt = k_p R_{0\cdot} (1 - \alpha_c) \quad (13)$$

$$C_B = k_B/k_p \quad (14)$$

where C_B is the chain transfer constant for B groups with either $R_B\cdot$ or $R_c\cdot$

radicals. Combining these with EQUATION (3a) we obtain

$$y_0' = \frac{2(k_t/k_p^2)(d\alpha_c/dt)_0}{C_B B_0} \quad (3b)$$

For a given system wherein the rate constants in this equation are fixed, the lowest value of y_0' may be achieved by using the lowest values for the initial rate, $(d\alpha_c/dt)_0$, and the highest concentration of active sites (B_0) that are practicable. Reasonable values for these limits are 5 per cent/hr. for the rate, and 5 or 0.5 moles/liter for B_0 , depending on whether the backbone chain contains an active site on every structural unit, or on every tenth (on the average) such unit. These upper limits on B_0 are based on the assumption that the initial mixture has a density of 1 and contains no more than 50 per cent by weight of the backbone polymer, the structural units of the latter being assumed to have a molecular weight of 100.

TABLE 2
GRAFT COPOLYMERIZATION PARAMETERS FOR VARIOUS MONOMERS (60°)
 $B_0 = 0.5$ moles/liter; $(d\alpha_c/dt)_0 = 5\%$ /hr.

Monomer	k_t/k_p^2 from Ref. (1)*	$C_B = 1$		$C_B = 10^{-1}$		$C_B = 10^{-2}$		$C_B = 10^{-3}$	
		y_0'	ϵ_0	y_0'	ϵ_0	y_0'	ϵ_0	y_0'	ϵ_0
Styrene	1160	6.5×10^{-2}	0.97	6.5×10^{-1}	0.76	6.5	0.24	65	0.03
Methyl methacrylate	70	3.9×10^{-3}	1	3.9×10^{-2}	0.98	3.9×10^{-1}	0.84	3.9	0.34
Vinyl acetate	5.4	3.0×10^{-4}	1	3.0×10^{-3}	1	3.0×10^{-2}	0.99	3.0×10^{-1}	0.87
Methyl acrylate	1.1	6.1×10^{-5}	1	6.1×10^{-4}	1	6.1×10^{-3}	1	6.1×10^{-2}	0.97

* Mole sec liter⁻¹.

A concrete evaluation of the conditions for gelation according to this analysis can now be made for various monomers. In TABLE 2 are shown values of y_0' calculated by EQUATION (3b) for four common monomers, at polymerization conditions considered to be of practical interest, for values of C_B ranging from 1 to 10^{-3} . Values of the termination and propagation rate constants (in liter mole⁻¹ sec⁻¹) are those given by Matheson and coworkers for 60°. It is important to note that the ratio k_t/k_p^2 for different monomers varies over a 1000-fold and is lowest for vinyl acetate and methyl acrylate. For this reason, it is easier to get low values of y_0' for the latter monomers, hence they provide ideal media for obtaining highly efficient graft copolymerizations without gelation.

In order to appreciate the limitations on gelation imposed by the values of y_0' given in TABLE 2, it is necessary to take into account the fact that polymerization is never complete in practice. The degree of completion of polymerization, α_c , is simply related to the degree of completion of the branching reaction, α_B . Thus, combining EQUATIONS (5) and (13) and integrating:

$$(1 - \alpha_B) = (1 - \alpha_c)^{C_B} \quad (15)$$

Accordingly, if C_B is very small, the degree of completion of the branching reaction is small even when the polymerization is almost completed. In TABLE

3 are shown values of α_B where $\alpha_c = 0.95$ and the corresponding values of n_B required for gelation for various monomers, calculated for the polymerization conditions and y_0' values of TABLE 2. From this table, it appears that, under the conditions of practical interest chosen here, gelation is not likely to occur, except for styrene or methyl methacrylate at a high value of C_B , unless n_B is very large. This latter condition would be met in the event that high molecular weight homopolymers with an active transfer site on each unit were employed as backbone chains. (This is actually the case which obtains in the homopolymerization of methyl acrylate to be discussed later).

Styrene appears to be the least attractive monomer for graft copolymerization at 60°, because of the ease of gelation at high values of C_B , and because of the inefficiency of graft copolymerization at low values of C_B . This is, of course, due to the very high value of k_t/k_p^2 characteristic of this monomer.

Two additional factors operate to make the critical values of n_B for gelation

TABLE 3
CONDITIONS REQUIRED FOR GELATION FOR GRAFT COPOLYMERIZATION WITH VARIOUS
MONOMERS AT 95% CONVERSION (60°)
($B_0 = 0.5$ moles /liter; $(d\alpha_c/dt)_0 = 5\%/hr.$)

Monomer	Critical values of n_B required for gelation			
	$C_B = 1$ $\alpha_B = 0.95$	$C_B = 10^{-1}$ $\alpha_B = 0.26$	$C_B = 10^{-2}$ $\alpha_B = 0.03$	$C_B = 10^{-3}$ $\alpha_B = 0.003$
Styrene	9	16	292	22,300
Methyl methacrylate	90	93	164	2,060
Vinyl acetate	1120	1110	1160	1,880
Methyl acrylate	5500	5460	5450	6,140

in graft copolymerization under the chosen conditions even larger.† First, at the high polymer concentrations which are visualized for graft copolymerization, the effect of the high viscosity in lowering the diffusion constants for the free radicals will undoubtedly be sufficient to lower appreciably the value of k_t ,^{1, 14} thus reducing the value of y_0' and making the values of n_B in TABLE 3 higher at most of the conditions here considered. Secondly, the above treatment neglects the effects of monomer transfer. Although integration of EQUATION (6) leads to expressions too cumbersome for practical calculations when monomer and solvent transfer are not negligible, in first approximation the condition for gelation in this case may be taken as

$$n_B \geq \frac{2k_t R_0 \cdot + k_m C_0 + k_s S_0}{2k_t R_0 \cdot Z^*} \quad (\text{approximately}) \quad (16)$$

where Z^* is given by EQUATION (9) with y_0 of EQUATION (3) replacing y_0' . As long as y_0 is much smaller than unity, as required for efficient graft copolymerization, the implication of this equation is that the greater the magnitude of the factors which tend to decrease the average molecular weight, the lower is

† A third factor may be that termination may occur partly by disproportionation.

the probability of gelation. Values of n_B calculated by EQUATION (16) taking into account chain transfer with monomer would not be significantly higher than those of TABLE 3 except for vinyl acetate and methyl acrylate for $C_B < 1$.

In the preceding discussion, it was assumed that the number of chain transfer sites per chain, n_B , is the same for all chains of parent polymer. If this is not the case, gelation involving the chains with the largest number of transfer sites will occur first. In order to account for this, an average value of n_B giving greater weight to the higher than to the lower values should be employed in EQUATION (11). By analogy with the treatment of gelation in vinyl-divinyl polymerizations,⁸ it appears that the use of a weight average n_B should be a sufficiently good approximation for our present purposes. This probably is not so for the homopolymerizations to be considered below.

If the branching sites on the backbone polymer are closely spaced, the probability of transfer or of termination with other sites or radicals, respectively, on the same chain will be greater than given by the rates in TABLE 1, since the density of these sites in the neighborhood of each branch radical is greater than the average density. Zimm and Bragg have analyzed an analogous problem.¹⁵ An extension of this analysis to the problem at hand shows that, under suitable conditions, microgelation may occur by mutual termination of branch radicals on the same parent chain, at conversions lower than those predicted by EQUATION (11) for macrogelation. This observation is also of particular interest in the case of homopolymerization discussed below.

Other methods for preparing graft copolymers by the free radical polymerization of a monomer in the presence of a backbone chain which do not require chain transfer reactions may also be considered. For example, the parent polymer may contain n_B hydroperoxide groups on each chain, whose decomposition will lead to the growth of branches. It is easily shown that if no transfer agents are added and if transfer with monomer is neglected the condition for gelation is

$$\alpha_B > \frac{2}{n_B} \quad (17)$$

or

$$-\ln(1 - \alpha_c) > \frac{2k_p}{\sqrt{k_i k_t}} \sqrt{B_0/n_B} \quad (18)$$

where α_B is the fraction of hydroperoxide groups which have initiated polymerization, α_c is the fractional conversion of monomer to polymer, k_i is the effective initiation constant for the hydroperoxide-monomer pair, B_0 is the total initial concentration of hydroperoxide groups in the system, and the other rate constants are defined as before. Another method for graft copolymerization would be to employ a backbone chain possessing n_B polymerizable double bonds either in or attached to each chain. If transfer reactions are neglected and if the reactivities of the groups attached to the chain are the same as those of the monomer, it can be shown that gelation occurs when

$$\alpha_c > \frac{1}{2n_B} \quad (19)$$

It appears that, unless transfer agents are added, these methods of graft copolymerization, especially the latter, are more likely to lead to gelation than the one considered previously.

Homopolymerization

If chain transfer by means of a reaction of type (IV) is responsible for branching, then the mechanism of crosslinking is analogous to that previously discussed for graft copolymerization, except that the concentration B of chain transfer sites increases as the polymerization progresses and is approximately equal to $\alpha_c C_0$. The number of branching sites per chain, which is identical in this case with the degree of polymerization, is not the same for all chains, and a suitable average value must be chosen for the purpose of the present analysis. By analogy with the case of vinyl-divinyl copolymerization, the weight average will be used as a first approximation,⁸ even though it appears that this is only a crude approximation in this case. Proceeding in a manner analogous to that followed for graft copolymerization, neglecting monomer transfer* and solvent transfer:

$$R_{B\cdot} = \frac{R_0 \cdot \alpha_c}{x_0 + \alpha_c} \quad (20)$$

where:

$$x_0 = \frac{2k_t R_0 \cdot}{k_B C_0} = \frac{2(k_t/k_p^2)(d\alpha_c/dt)_0}{C_B C_0} \quad (21)$$

The concentration of crosslinks, X , is defined by

$$\frac{dX}{dt} = \frac{k_t R_0^2 \alpha_c^2}{(x_0 + \alpha_c)^2} \quad (22)$$

Time may be eliminated through the equation:

$$\frac{d\alpha_c}{dt} = k_p R_0 \cdot (1 - \alpha_c) \quad (23)$$

Accordingly:

$$\frac{dX}{d\alpha_c} = \frac{k_t R_0 \cdot}{k_p} \cdot \frac{\alpha_c^2}{(1 - \alpha_c)(x_0 + \alpha_c)^2} \quad (24)$$

Integrating:

$$X = \frac{1}{2} C_0 C_B Z' \quad (25)$$

Where:

$$Z' = x_0 \left\{ \left[\frac{1}{(1 + x_0)^2} - 1 \right] \log_e \left(\frac{x_0 + \alpha_c}{x_0} \right) - \frac{1}{(1 + x_0)^2} \log_e (1 - \alpha_c) + \frac{x_0 \alpha_c}{(1 + x_0)(\alpha_c + x_0)} \right\} \quad (26)$$

and $C_B = k_B/k_p$.

* This assumption introduces an error particularly in the case of methyl acrylate and vinyl acetate; the effect of monomer transfer in this case will be discussed later.

Again, using the previously mentioned condition for gelation, since the total number of chains is $\alpha_c C_0 / \bar{n}_B$, the requirement for gelation is that:

$$\bar{n}_B > \frac{\alpha_c}{C_B Z'} \quad (27)$$

In FIGURE 2, the quantity (α_c/Z') is plotted as function of x_0 for various values of α_c . The results are very similar to those in FIGURE 1, hence the discussion of the relationships in that figure is largely applicable here. One difference, however, is that for $\alpha_c = 1$, $\alpha_c/C_B Z' = 0$ and, accordingly, at complete conversion the condition for gelation is always satisfied. This result may not be

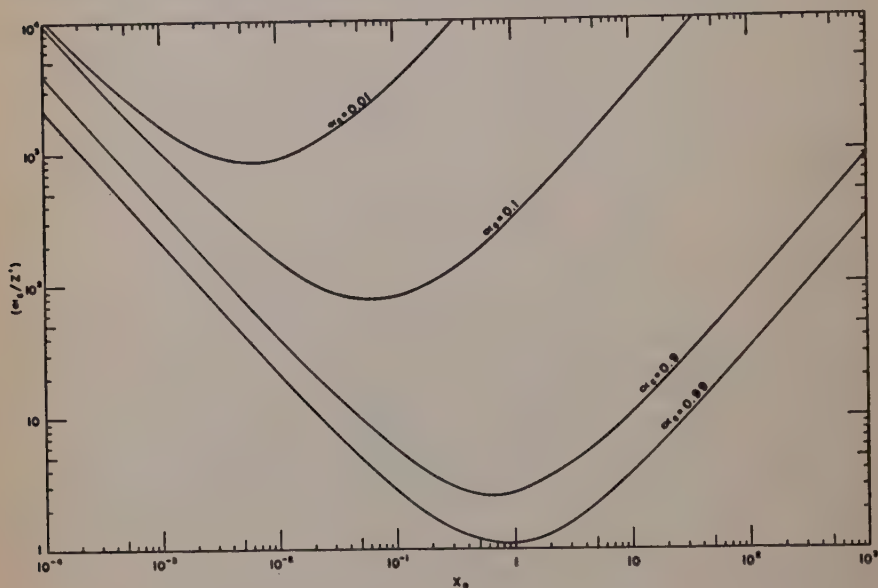


FIGURE 2. Gelation parameters in vinyl homopolymerization.

quite correct, since the free radical concentration $R_0\cdot$ must decrease when the polymerization is about complete, unless the termination rate vanishes, the initiation rate vanishing as soon as all the monomer is consumed. This vitiates the integration of EQUATION (24), which was carried out assuming constant value of x_0 and therefore also of $R_0\cdot$. In any event, this result is of no practical interest, since in practice no polymerization is ever absolutely complete.

To illustrate the results of this analysis at value of α_c less than unity, the critical values of \bar{n}_B required for gelation (TABLE 5) were calculated from EQUATION (25) for the polymerization of each of several monomers at 60° at an initial rate of 5 per cent/hr. These are to be compared with corresponding values of the weight average degree of polymerization, \bar{P}_w , which are expected to obtain under these conditions. The latter were calculated: (1) with the assumption that all of the rate constants are independent of the conversion

and (2) ignoring the effects of branching on the molecular weight distribution. The values of the rate constants employed in this calculation are given in TABLE 4, together with the sources from which the constants were taken or

TABLE 4
KINETIC CONSTANTS FOR VARIOUS MONOMERS AT 60°C
(Rate constants in liter mole⁻¹ sec⁻¹; transfer constants dimensionless)

Monomer	From ref. 1					
	$k_t \times 10^{-7}$	k_p	C_M	Reference	C_B	Reference
Methyl methacrylate	0.94	367	10 ⁻⁵	(13c) (16)	ca. 10 ⁻⁵	Estimated†
Styrene	3.6	176	6 × 10 ⁻⁵	(13a)	8 × 10 ⁻⁵	(17)**
Vinyl acetate	7.4	3700	2.5 × 10 ⁻⁴	(6)*	3.1 × 10 ⁻⁴	(18)(1)††
Methyl acrylate	0.48	2090	ca. 10 ⁻⁵	(3)†	8 × 10 ⁻⁴	(6)*
					4 × 10 ⁻⁴	(18)(1)††
					ca. 10 ⁻⁴	(7)***

* The values of C_M and C_B for vinyl acetate are taken from Stockmayer *et al.*⁶; they are in good agreement with corresponding values extrapolated from the data of Wheeler *et al.*⁶ at 70°.

† Estimated from the intrinsic viscosity (ca. 6) for the soluble portion of thermally polymerized methyl acrylate.

‡ On the basis of structural considerations, the transfer constant for polymethyl methacrylate would be expected to be lower than that for the monomer, since the latter results in free radicals stabilized by allylic type resonance. A value of C_B smaller than 10⁻⁵, however, would be quite unusual, and accordingly this value is tentatively accepted.

** This value is the chain transfer constant of styrene with isopropyl benzene at 60°. It would be expected that steric effects would result in a slightly higher transfer constant with polystyrene than with isopropyl benzene. Therefore the value 10⁻⁴ will be used.

†† The value $k_B = 0.054$ is obtained by extrapolating to 60° the data of reference (18) at 130° and 154°, using the activation energy of 7 kcal/mole obtained therein. The result is combined with k_p of reference (1) to give C_B .

*** Estimated by extrapolation of the data of reference (7) on the chain transfer constants in methyl acrylate at 30° of model compounds resembling the structure of polymethyl acrylate.

TABLE 5
CONDITIONS FOR GELATION IN THE HOMOPOLYMERIZATION OF VARIOUS MONOMERS AT 60°C
($d\alpha_c/dt$)₀ = 5%/hr.

Monomer	x_0 calc'd by eq. (21)	Critical \bar{n}_p for gelation calc'd. by eq. (27)		Calc'd. \bar{P}_w	Predominant reaction limiting calc'd. \bar{P}_w
		$\alpha_c = 0.01$	$\alpha_c = 0.99$		
Methyl methacrylate	19	6 × 10 ¹⁰	7 × 10 ⁵	1.6 × 10 ⁴	Radical combination
Styrene	31	9 × 10 ⁹	1 × 10 ⁵	10 ³	Radical combination
Vinyl acetate	1.8 × 10 ⁻²	1.4 × 10 ⁶	2 × 10 ⁴	8 × 10 ³	Monomer transfer
Methyl acrylate	3.0 × 10 ⁻²	1.5 × 10 ⁷	8 × 10 ⁴	2 × 10 ⁵	Monomer transfer

estimated. In some cases, these values, especially those for C_B , are not accurately known at the present time. In spite of this and in spite of the use of the aforementioned simplifying assumptions, it is believed that the results given in TABLE 5 are sufficiently good for our present purpose of illustrating the relative tendency of the various monomers to undergo gelation. Obviously, more precise theoretical treatment and more precise evaluation of the pertinent

rate constants for monomers of different structures, over wide ranges in temperature, will be needed for an accurate detailed understanding of branching and gelation in various polymers.

The calculated values of x_0' and the corresponding values of \bar{n}_B for 1 per cent and 99 per cent conversion of the various monomers are given in TABLE 5 with the calculated \bar{P}_w 's which should obtain at low conversions.*

It may be seen that, according to the analysis here presented, gelation will not occur in methyl methacrylate or styrene even at 99 per cent complete conversion. In fact, the discrepancy between \bar{P}_w and \bar{n}_B critical in these two cases is so great that neither the marked decrease in the termination constant k_t for methyl methacrylate nor the lesser decrease in k_t for styrene observed with increasing conversion^{1, 14} would increase \bar{P}_w sufficiently to cause gelation even at 99 per cent conversion. On the other hand, gelation is predicted to occur for vinyl acetate at a high conversion (ca. 99 per cent) and for methyl acrylate at a relatively low conversion (ca. 80 per cent). These results are in qualitative agreement with the experimental findings, although methyl acrylate is known to form insoluble polymer at even lower conversions.

The absence of any tendency for gelation in the homopolymerization of methyl methacrylate results from the low values of both k_p and C_B for this monomer. The low value of k_p requires that R_0 must be abnormally high to achieve the specified rate of polymerization. This coupled with the low rate of branching (low C_B) results in a high value of x_0 and correspondingly the critical values of \bar{n}_B required for gelation are higher than for the other monomers. At the same time, the low value of k_p causes \bar{P}_w for the given rate of polymerization to be lower than for any of the other monomers except styrene. These considerations imply that the polymer prepared in the absence of chain transfer agents is more nearly linear for methyl methacrylate than for any of the other three monomers.

The principal difference between styrene and methyl methacrylate is the higher tendency for branching (higher C_B) for the former. In spite of this, the low \bar{P}_w obtained for styrene does not exceed the moderately high value of \bar{n}_B required for gelation at 99 per cent conversion. It can be said that failure of styrene to gel results from its very low propagation constant, rather than from the absence of a branching reaction.

The higher values of k_p and of C_B for vinyl acetate are such that the value of x_0 for this monomer is near the minimum in the curves of FIGURE 2. Hence, the values of \bar{n}_B required for gelation are lower for this than for any of the other monomers. The absence of gelation except at high conversions is a consequence of the very low values of \bar{P}_w which result from the very high value of C_M in this case.

Finally, methyl acrylate differs from methyl methacrylate in that branching is more probable (C_B is higher), from styrene in that the propagation constant is an order of magnitude higher, and from vinyl acetate in that chain transfer with the monomer is less frequent. The result is that x_0 is low for this monomer, but lower than the optimum for gelation (FIGURE 2), and correspond-

* The critical values of \bar{n}_B would be higher if termination occurred partly by disproportionation.

ingly the critical values for \bar{n}_B are moderately high. The very high value of k_p^2/k_t and the low value of C_M , however, are such that exceptionally high molecular weights obtain. The ability of methyl acrylate to undergo gelation at low conversion is, therefore, a combined result of its ability to polymerize to very long chains and of the great tendency of the alpha hydrogen on each unit of these chains to undergo chain transfer.

The tendency for gelation may be altered by changing certain of the experimental conditions. Thus, according to EQUATION (21), x_0 may be altered by choosing some other rate of polymerization. For practical purposes, it is unlikely that this rate could be changed enough either to prevent the gelation of methyl acrylate or to cause gelation to occur for methyl methacrylate or styrene. Gelation can be prevented, in bulk polymerizations, by the addition of sufficient amounts of an active transfer agent. In so far as the pertinent rate constants are sensitive to temperature, the tendency toward gelation will be a function of the temperature of polymerization.

Problems for Future Consideration

The analysis presented above is a preliminary one which suffices to show that crosslinking and gelation may occur in vinyl polymerization by the simultaneous action of chain transfer branching and of the termination of free radicals by combination. The predictions based on this treatment should be fairly accurate in the case of graft copolymerization, but the experimental data are not available with which they might be tested. Comparison of the results of the analysis for homopolymerizations with experiment shows them to be at least qualitatively correct. The discrepancy between the predicted ($\alpha = 0.80$) and observed ($\alpha < 0.05$) macrogel point for methyl acrylate at 60° is no greater than may be expected from consideration of the approximations made in the treatment.

The most drastic simplification in the treatment of graft copolymerization here presented consists of neglecting monomer transfer. According to the approximate EQUATION (16), the error thus introduced decreases in the order: VA > MA \gg MMA > S. The effect on the probability of gelation of the dependence of the termination rate constant on the viscosity of the medium should also be considered. The error which may have been introduced by using a weight average value of n_B when this quantity is not the same for all backbone chains appears to be too small in the case of graft copolymerizations to warrant further consideration. A more exact and detailed account of the problem of crosslinking in graft copolymerization will be given in a future publication.

The error in the treatment of crosslinking and gelation in homopolymerization may arise from the neglect (except in the calculation of the actual molecular weight) of monomer transfer, and, particularly, by the failure to consider the effects of branching on the molecular weight distribution in the calculation of the average degree of polymerization. Moreover, the use of a weight average degree of polymerization in the criterion for gelation is at best a crude approximation since it does not account sufficiently for the fact that the longer chains

branch preferentially. The dependence of the termination rate constant on conversion also must be considered in calculating the conditions for gelation at high conversions.

Another important factor, which may lead to microgelation and to the production of inhomogeneous insoluble polymers (popcorn polymers), is that, under some conditions, the concentration of segments of the same chain in the neighborhood of a given branch radical may be much higher than the average concentration of polymer segments. In this case, crosslinking by self termination of branch radicals growing on the same backbone chain may occur with greater probability than termination with other free radicals, and small crosslinked networks (microgel particles) may result. For methyl acrylate, by the extension of a similar analysis of Zimm and Bragg,¹⁵ it is estimated that even at 1 per cent conversion a significant fraction of the polymer consists of these small crosslinked networks. It is believed that these may act as the seeds for the inhomogeneous growth of an infinite crosslinked network.³

Several of the above problems have already proved to be amenable to calculation. For example, we have determined the molecular weight distribution to be expected for polymerization with branching by the mechanism of reaction (IV). It is expected also that an approximate estimate of the effect of the dependence of k_t on α can be made. However, the treatment of intramolecular reactions still requires considerable improvement, particularly in taking proper account of the increased density of chain segments resulting from branching. Finally the proper criterion of gelation applicable to the problems here considered remains to be determined. It is the authors' intention to present in the near future the results of these more detailed considerations.

Summary and Conclusions

A simplified analysis of the kinetics of crosslinking by branching has been carried out for the cases of (a) graft copolymerization and (b) homopolymerization.

This analysis shows that gelation by chain transfer branching in graft copolymerization is impossible under ordinary practical conditions when the monomer is methyl acrylate, vinyl acetate, or methyl methacrylate. It is possible when styrene is the monomer, if the number of potential chain transfer sites per chain of backbone polymer is moderately high.

According to the present simplified theory, gelation by chain transfer branching in bulk homopolymerization is impossible in methyl methacrylate, styrene, and vinyl acetate. In the case of vinyl acetate at high conversions, however, the criterion of gelation is so nearly fulfilled that it appears that a more refined theory would predict gelation to occur under suitable conditions.

The present theory would indicate that gelation would occur in bulk homopolymerization of methyl acrylate at conversions of the order of 80 per cent. Actually, it is found experimentally that in this case gelation normally occurs at conversions as low as 5 per cent or lower. Refinements of the theory which would lead to better agreement with the experimental results are outlined.

Acknowledgment

The authors are greatly indebted to Mr. Harry F. Mason for valuable assistance in carrying out the calculations for FIGURES 1 and 2. The help of Miss Helen P. Wasserman and Mrs. Ethel M. Schuele is also gratefully acknowledged. The authors wish to thank Doctor P. J. Flory of Cornell University and Doctor F. M. Rugg of the Bakelite Company for making available some of their results in advance of publication.

References

1. MATHESON, M. S., E. E. AUER, E. B. BEVILACQUA, & E. J. HART. 1951. *J. Am. Chem. Soc.* **73**: 5395-5400.
2. SCHILDKNECHT, C. E. 1952. *Vinyl and Related Polymers*. (4): 244-246. Wiley. N. Y.
3. PANCHAK, J. R., T. T. KRYZA, & T. G. FOX. 1952. Paper presented before the 122nd Meeting of the American Chemical Society.
4. BREITENBACH, J. W. & A. FALLY. 1951. *Monatsh. für Chemie*. **82**: 1118.
5. BLAICKIE, K. G. & R. N. CROZIER. 1936. *Ind. Eng. Chem.* **28**: 1155; WHEELER, O. L. 1953. *Ann. N. Y. Acad. Sci.* **57** (4): 360.
6. WHEELER, O. L., E. LAVIN, & R. N. CROZIER. 1952. *J. Polymer Sci.* **9**: 157; STOCKMAYER, W. H., J. T. CLARKE, & R. O. HOWARD. 1952. Paper presented at the 121st Meeting of the American Chemical Society.
7. OSTERHELD, J. E. & P. J. FLORY. Cornell University. Private communication.
8. FLORY, P. J. 1941. *J. Am. Chem. Soc.* **63**: 3083, 3091, 3096; STOCKMAYER, W. H. 1943. *J. Chem. Phys.* **11**: 45, 393; 1944. *Ibid.* **12**: 125.
9. RUGG, F. M., J. J. SMITH, & L. H. WARTMAN. 1953. *Ann. N. Y. Acad. Sci.* **57** (4): 398.
10. ALFREY, T., JR., J. J. BOHRER, & H. MARK. 1952. *Copolymerization, High Polymers*. **8**(8): 156-160. Interscience. N. Y.
11. CARLIN, R. B. & N. E. SHAKESPEARE. 1946. *J. Am. Chem. Soc.* **68**: 876; CARLIN, R. B. & D. L. HUFFORD. 1950. *Ibid.* **72**: 4200.
12. ALFREY, T., JR. & D. BANDEL. 1952. *Copolymerization, High Polymers*. **8**(8): 159-160. Interscience. N. Y.
13. MAYO, F. R., R. A. GREGG, & M. S. MATHESON. 1951. *J. Am. Chem. Soc.* **73**: 1691; ARNETT, L. M. 1952. *Ibid.* **74**: 2027; ARNETT, L. M. & J. H. PETERSON. 1952. *Ibid.* **74**: 2031; BAYSAL, B. & A. V. TOBOLSKY. 1952. *J. Polymer Sci.* **8**: 529; *Ibid.* **9**: 171.
14. TROMMSDORFF, E. B.I.O.S. Report No. 363, Item 22; SCHULZ, G. V. & G. HARBORTH. 1947. *Makro. Chem.* **1**: 106. (For a discussion of the Norrish-Trommsdorff effect see C. E. Schildknecht, 1952. *Vinyl and Related Polymers*: 191-196. Wiley. N. Y.)
15. ZIMM, B. H. & J. K. BRAGG. 1952. *J. Polymer Sci.* **9**: 476.
16. O'BRIEN, J. L. & F. GORNICK. 1953. Paper presented before the 123rd Meeting of the American Chemical Society.
17. GREGG, R. A. & F. R. MAYO. 1947. *Disc. Faraday Soc.* **2**: 328.
18. BEVINGTON, J. C., G. M. GUZMAN, & H. W. MELVILLE. 1952. *Nature*. **170**: 1026.

THE STRUCTURE OF AMYLOPECTIN AND GLYCOGEN

By Charles O. Beckmann

Department of Chemistry, Columbia University, New York, N. Y.

Introduction

At the present time, more detailed knowledge of the structure of amylopectin, the branched fraction of starch, and of glycogen, its counterpart in animals, is available than for any other branched polysaccharide. The present discussion will therefore be limited to these substances. It is known that both materials are composed of the same monomer unit, anhydro-glucose, that the main chains are held together by α -1,4 glucosidic linkages and that branches occur at α -1,6 glucosidic linkages (FIGURE 1). Amylopectin and glycogen differ structurally only in the ratio of α -1,6 links to α -1,4 links; which ratio lies between $1/18$ to $1/27$ for amylopectin from various sources and $1/10$ to $1/18$ for glycogen from various sources.

The chemical methods of methylation and periodate oxidation enable one to determine the fraction of terminal glucose units in the molecule, *i.e.*, glucose units which have the 4-position free (FIGURE 2). The enzymatic method recently reported by Larner, Illingworth, Cori and Cori^{1, 2} enables one to determine not only the fraction of branch units in the molecule, but by stepwise degradation, using the enzymes phosphorylase and α -amylglucosidase alternately, to determine the average structure of the successive tiers.

Before proceeding with a description of the various methods, it may be desirable to consider the three models which have been proposed for amylopectin and glycogen and which are shown diagrammatically in FIGURE 3. The Staudinger model^{3, 4} consists of a long chain of glucoses bound by α -1,4 links with unbranched side chains attached to the main chain at branch points by α -1,6 links. The Haworth model^{5, 6} consists of a number of chains, which are attached one to the next one at branch points by α -1,6 links, so that each chain has but one branch point. The Meyer model^{7, 8} consists of a combination of the two so that each chain may branch further whether its origin be a 1,4 or a 1,6 link at the branching glucose.

A clearer description of the three models may be obtained by defining a chain specifically as a segment of glucose residues bound by α -1,4 links starting from a branching glucose or from an aldehyde glucose, and terminating at another branching glucose or at a terminal glucose. Following Sillén and Myrbäck,⁹ a chain originating at a 1,4 link will be called an L-chain, a chain originating at a 1,6 link will be called a Q-chain, and one originating at an aldehyde glucose will be called an A-chain. Since there is but one free aldehyde group to each molecule (A in FIGURE 3) and this may be taken as the starting point in developing the model of the molecule, then for the molecule to be branched, the A-chain is necessarily branched, and this statement will be omitted from the characterization of each model. Thus, in these terms, one may say that, in the Staudinger model, only L-chains may terminate in a branch; in the Haworth model, only Q-chains may terminate in a branch; and, in the Meyer model, both L- and

Q-chains may terminate in a branch. In the "ideal" Meyer model shown in FIGURE 3, the number of L-chains branched is equal to the number of Q-chains branched. It is obvious from this point of view that the Meyer model is the most general, and that many models are possible by varying the fraction, f , of L-chains which branch. Then the Haworth model is the extreme case of the

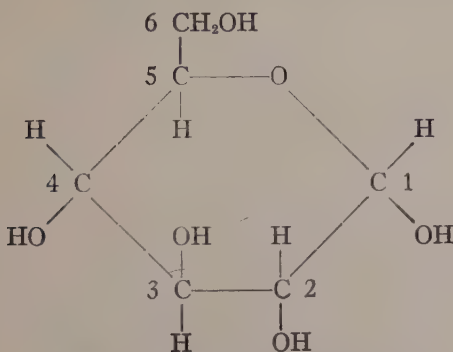


FIGURE 1. Structural formula of D-glucose.

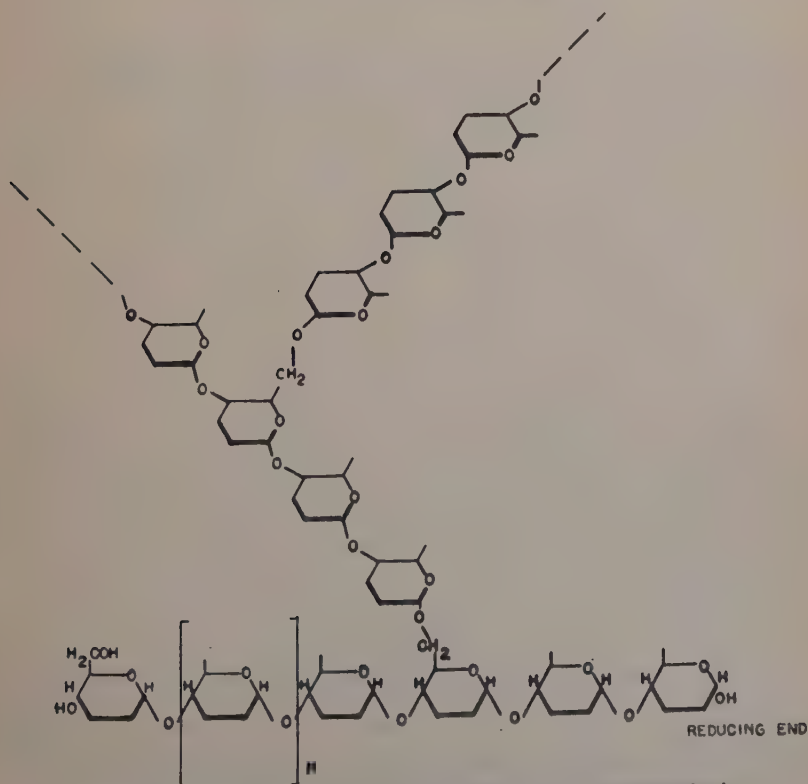
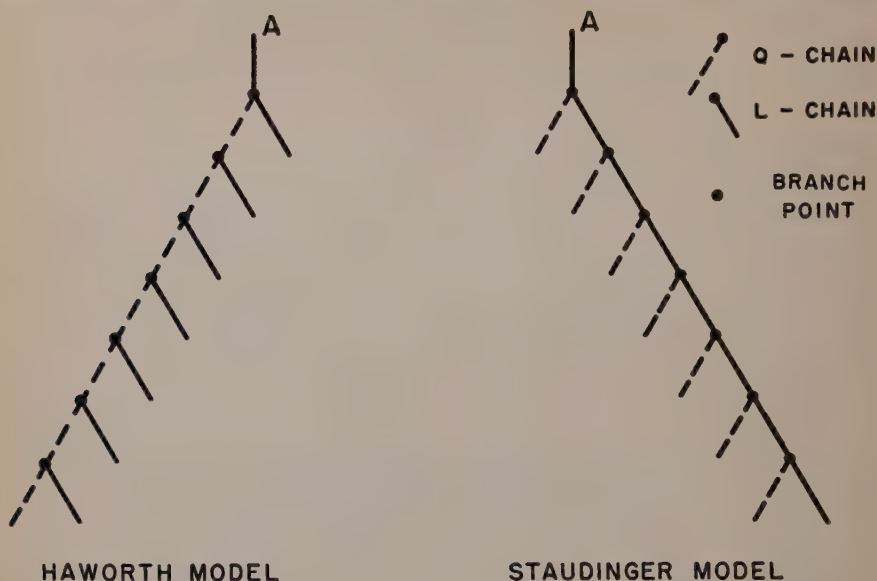


FIGURE 2. Structural formula of a section of the glycogen or amylopectin molecule.

Meyer model for which $f = 0$ and the Staudinger model is the other extreme case for which $f = 1$. The factor, f , is not only convenient for characterizing



IDEAL MEYER MODEL

FIGURE 3. Diagrammatic representations of proposed models for amylopectin and glycogen.

these models but, as will be shown below from the work of Larner, Illingworth, Cori and Cori² is an experimentally attainable quantity for characterizing the structure of the successive tiers of branched polysaccharide molecules.

It should be emphasized that the definition of a "chain" given above deviates from the definition of the term as used by polysaccharide chemists¹⁰ but is consistent with the definition of the term as used by polymer chemists.^{11, 12} This is obvious from the following considerations.

If C is the number of chains (as defined above), E , the number of end groups and B , the number of branching glucoses in a molecule containing a total of N glucoses, then for any model it is seen that:

$$C = 2B + 1$$

$$E = B + 1$$

and

$$\frac{E}{C} = \frac{B + 1}{2B + 1} \cong \frac{1}{2}^*$$

Further, if \bar{n} is the average chain length and $\beta (= B/N)$ is the fraction of branching glucoses in the molecule, then

$$\bar{n} = \frac{N}{C} = \frac{N}{2B + 1} \cong \frac{N}{2B} = \frac{1}{2\beta} \quad (1)$$

The reciprocal of the fraction of end groups, which is the definition usually used by the polysaccharide chemist for the "average chain length," is actually the sum of the average chain length for the outer chains, \bar{n}_0 , and that for the interior of the molecule, \bar{n}_i . If N_0 is the total number of glucoses in the outer chains then this statement follows from:

$$\frac{N}{E} = \frac{N}{B + 1} \cong \frac{N}{B} = \frac{N_0}{B} + \frac{N - N_0}{B} \cong \frac{N_0}{E} + \frac{N - N_0}{C - E} \quad (2)$$

or

$$\frac{1}{\beta} = \bar{n}_0 + \bar{n}_i = 2\bar{n}$$

The Chemical End-Group Methods

The earliest end-group method used was that of methylation.^{13, 14, 15} By suitable methods, the free hydroxyl groups of amylopectin or glycogen were converted to methoxyl groups. On hydrolysis of the methylated product, a mixture of methylated glucoses was obtained, fractionated and analyzed by various methods. A branching glucose gives rise to 2,3-dimethyl glucose, a chain glucose to 2,3,6-trimethyl glucose, and a terminal glucose to 2,3,4,6-tetramethyl glucose. The mole fraction of the latter in the mixture is equal to β . From this value and EQUATION (1), the average chain length, \bar{n} , may be calculated.

The more recently developed end group method of periodate oxidation^{13, 14, 15} is more easily carried out experimentally and has given results which are in good

* The approximation used throughout is that terms of the order $1/B$ and $1/N$ are negligible and is valid if the molecule is large or the precision of measurement less than $1/B$.

agreement with those obtained from methylation studies. Periodate ion will attack the glucose ring, oxidizing the central of three adjacent —CHOH groups to formic acid. Since this structure exists in each terminal glucose of amylopectin or glycogen where the 2,3,4 hydroxyls are unsubstituted, the titration of the formic acid formed on oxidization gives a measure of the fraction of end groups. The reaction is somewhat complicated by the fact that the glucose at the aldehyde end is oxidized to one molecule of formaldehyde and two molecules of formic acid, but in a large, highly branched molecule this contribution of formic acid may be neglected.

The Enzymatic End Group Method

The methods discussed in the above section enable one to obtain but a very limited concept of the branched polysaccharide molecules and, on the basis of these methods alone, one cannot select the correct structure from among the three that have been proposed for amylopectin and glycogen (FIGURE 3). Recently, G. T. Cori and J. Larner¹⁶ discovered a new enzyme, α -amyloglucosidase, and have shown that it will act *only* on a Q-chain consisting of a single glucose unit.¹⁷ The substrate for this enzyme is the limit dextrin produced from amylopectin or glycogen by the action of phosphorylase.

Phosphorylase catalyzes the degradation of amylopectin or glycogen in the presence of phosphate ion to form glucose-1-phosphate and a high molecular weight limit dextrin which is resistant to the further action of phosphorylase. The mechanism established for the reaction consists of splitting out glucose units as glucose-1-phosphate one at a time, beginning at the terminal end of a chain and stopping near the α -1,6 link of the branch point. Hestrin¹⁸ has shown that the limit dextrin, so formed, may be degraded further by the enzyme β -amylase, which also will not proceed beyond a branch point, and has estimated from the extent of this further degradation, that approximately six glucose units remain at each outer branch point of the phosphorylase limit dextrin. Cori and Larner¹⁷ find that, when this limit dextrin is treated with α -amyloglucosidase, the only substance split out is glucose. After this action the residual high molecular weight substance is again susceptible to attack by phosphorylase. They conclude, therefore, that at each outer branch point of the phosphorylase limit dextrin, there is one glucose unit remaining on each outer Q-chain and about five units on each outer L-chain, and that the action of the α -amyloglucosidase is the removal of the single glucose on the Q-chain, thus destroying the branch point and uncovering a new outer chain susceptible to further attack by phosphorylase. This conclusion was verified by treating various samples of glycogen and amylopectin with phosphorylase and α -amyloglucosidase *simultaneously* and determining both the glucose-1-phosphate and the glucose in the reaction mixture.¹ If each glucose molecule arose from a branch point and each glucose-1-phosphate molecule from a chain, the ratio of the two quantities is the fraction of branching units in the molecule and, from EQUATION (1), is equal to the fraction of end groups. The results obtained agreed satisfactorily with the results of end group determinations by the methylation method and by the periodate method.

To obtain more detailed information about the structure of amylopectin and glycogen, Larner, Illingworth, Cori and Cori² devised a method for evaluating the average chain lengths of the successive tiers of the molecule. The method consists of subjecting the sample to the action of phosphorylase, determining the amount of glucose-1-phosphate formed, and estimating the average chain length of the first tier from this quantity and the end-group analysis of the original sample. This is followed by subjecting the limit dextrin (LD_1) to the action of α -amylglucosidase and determining the amount of glucose liberated. This action exposes the second tier of chains and enables one to repeat the cycle of enzymatic actions.

A detailed analysis of the method leads to equations which enable one to estimate the fraction of Q- and L-chains in each tier in addition to the average chain length.

The experimental data consists of the following quantities:

$e = \beta$ = fraction of end groups in the parent molecule = fraction of branch units in the parent molecule;

z_1 = fraction of parent substance degraded by phosphorylase to produce limit dextrin LD_1 ;

e_1 = fraction of end groups in LD_1 ;

X_1 = fraction of LD_1 degraded to glucose by α -amylglucosidase to produce $LD_1(g)$;

z_2 = fraction of $LD_1(g)$ degraded by phosphorylase to produce LD_2 ;

e_2 = fraction of end groups in LD_2 ;

X_2 = fraction of LD_2 degraded by α -amylglucosidase to produce $LD_2(g)$;

z_3 = fraction of $LD_2(g)$ degraded by phosphorylase to produce LD_3 ; etc.

In the following calculation, it is assumed that each external Q-chain is degraded by phosphorylase until a single glucose remains on the chain, that each external L-chain with five or more glucoses is degraded until five glucoses remain and that each external L-chain with less than five glucoses is unattacked. The composite of chains which are subject to attack by phosphorylase at the same time is called a tier. Using a symbolism similar to that of Sillén and Myrbäck,⁹ let q_{in} be the number of Q-chains in the i -th tier with n glucoses in each chain and l_{in} be the number of L-chains in the i -th tier with n glucoses; l_{i0} is then the number of glucoses which are branched at the 6-position but have no substituent at the 4-position, i.e., the number of L-chains of zero length; q_{i0} is the number of Q-chains which are attached to a 6-position but have no substituent at the 4-position. These also will be considered to have zero length.

The fraction of branch units in the original molecule is equal by EQUATION (2) to the fraction of end groups and the average chain length is given by EQUATION (1). If Z_1 is the number of glucose units split off by the first action of phosphorylase, then the fraction of the original molecule degraded to produce the limit dextrin LD_1 is:

$$z_1 = \frac{Z_1}{N}$$

Since no branch units or end groups have been eliminated by this action, the fraction of end groups in LD_1 is:

$$e_1 = \frac{B}{N - Z_1} = \frac{\beta}{1 - z_1} \quad (3)$$

Thus e_1 can be calculated from β and z_1 or can be measured independently. A comparison of the two values can serve as a check on the method.

Each Q_n -chain of the first tier has been reduced to a Q'_0 chain, *i.e.*, a chain of zero length. These are split off by the first action of α -amyloglucosidase to produce the dextrin $LD_1(g)$. The fraction of LD_1 degraded in this process is:

$$X_1 = \frac{q'_0}{N - Z_1} = \frac{\kappa'_0}{1 - z_1} \quad (4)$$

where

$$q'_0 = \sum q_{1n} + q_{10}$$

and

$$\kappa'_0 = \frac{q'_0}{N}$$

Throughout this work, the symbol \sum represents a sum taken from $n = 1$ to $n = \infty$ unless otherwise indicated.

The character of the tier as represented by the fraction of Q -chains, f_1 , in the tier is given by:

$$f_1 = \frac{\sum q_{1n} + q_{10}}{\sum q_{1n} + q_{10} + \sum l_{1n}} = \frac{q'_0}{E} = \frac{q'_0}{B} = \frac{\kappa'_0}{\beta} = \frac{X_1}{e_1} \quad (5)$$

and is directly calculable from experimental data.

The calculation of the average chain length in each tier is not possible unless one makes simplifying assumptions concerning the distribution of the length of chains. The difficulty arises because L -chains with five or less glucoses will not be detected in the first tier by phosphorylase degradation but will contribute to the number of glucoses split out in the second tier. Two assumptions will be examined: (1) all chain lengths in a tier are either (a) greater than five or (b) less than five; and (2) a random distribution of chain lengths exists in a tier.

Case 1: In this case, the number of glucose units split out by the first action of phosphorylase is given by

$$Z_1 = \sum nq_{1n} + \sum (n - 5)l_{1n} \quad \text{for } n > 5$$

$$Z_1 = \sum nq_{1n} \quad \text{for } n \leq 5$$

The average chain length of the first tier, \bar{n}_1 , will exclude the glucose on Q -chains attached directly to the 6-position of the branching glucose, since

they may be considered an inherent part of the branching unit. Thus

$$\begin{aligned}\bar{n}_1 &= \frac{\sum nq_{1n} + \sum nl_{1n}}{\sum q_{1n} + \sum l_{1n}} = \frac{Z_1 + 5 \sum l_{1n}}{B} \\ &= \frac{z_1}{\beta} + 5(1 - f_1) \quad \text{for } n > 5 \quad (6a)\end{aligned}$$

$$\bar{n}_1 = \frac{z_1}{f_1\beta} \quad \text{for } n \leq 5 \quad (6b)$$

Equation (6b) is valid only when the average chain length of the Q-chains is equal to that of the L-chains. If one wishes to include in the average the glucoses on the Q-chain which are part of the branch unit then the average chain length becomes

$$\begin{aligned}\bar{n}'_1 &= \frac{\sum (n+1)q_{1n} + \sum nl_{1n}}{\sum q_{1n} + \sum l_{1n}} = \frac{\sum nq_{1n} + \sum nl_{1n} + \sum q_{1n}}{B} \\ &= \frac{Z_1 + 5 \sum l_{1n} + \sum q_{1n}}{B} = \frac{z_1}{\beta} + 5(1 - f_1) + f_1 \quad \text{for } n > 5 \quad (7a)\end{aligned}$$

$$\bar{n}'_1 = \frac{z_1}{f_1\beta} + 1 \quad \text{for } n \leq 5 \quad (7b)$$

Case 2: If one assumes a random distribution of chain lengths in the tier, the fraction of the L-chains with $n \leq 5$ will not be attacked by phosphorylase. The fraction of L-chains, w_n , with length n is given by the equation

$$w_n = \frac{l_{1n}}{\sum l_{1n}} = \frac{1}{\bar{n}_1} \left(\frac{\bar{n}_1 - 1}{\bar{n}_1} \right)^{n-1}$$

For this case, the number of glucoses split by phosphorylase is

$$\begin{aligned}Z_1 &= \sum nq_{1n} + \sum_{n=5}^{\infty} (n-5)l_{1n} \\ &= \sum nq_{1n} + \sum (n-5)l_{1n} + \sum_{n=1}^5 (5-n)l_{1n} \\ &= \sum nq_{1n} + \sum nl_{1n} - 5l_{1n} + \sum_{n=1}^5 l_{1n} \sum_{n=1}^5 (5-n)w_n\end{aligned}$$

The average chain length in the tier is

$$\begin{aligned}\bar{n}''_1 &= \frac{\sum nq_{1n} + \sum nl_{1n}}{B} = \frac{Z_1}{B} + 5 \frac{\sum l_{1n}}{B} - R_1 \frac{\sum l_{1n}}{B} \\ &= \frac{z_1}{\beta} + 5(1 - f_1) - R_1(1 - f_1)\end{aligned} \quad (8)$$

where

$$R_i = \sum_{n=1}^5 (5 - n)w_{in} \cong \frac{1}{0.10\bar{n}_i + 0.12} \quad (9)$$

Again, if one wishes to include the branch glucose of the Q-chain, the average becomes

$$\bar{n}_1''' = \bar{n}_1'' + f_1 \quad (10)$$

After treatment of LD₁ with α -amylglucosidase, the resulting dextrin LD₁(g) is treated with phosphorylase to produce the limit dextrin LD₂. The fraction of glucose units split in this process is:

$$z_2 = \frac{Z_2}{N - Z_1 - q'_0} = \frac{Z_2}{N_1}$$

The fraction of branch units in LD₁(g) is:

$$\beta_1 = \frac{B - q'_0}{N - Z_1 - q'_0} = \frac{B_1}{N_1} = \frac{\beta - \kappa'_0}{1 - z_1 - \kappa'_0} = \frac{e_1 - X_1}{1 - X_1} \quad (11)$$

and the average chain length is therefore $\frac{1}{2}\beta_1$.

The fraction of end groups in the limit dextrin LD₂ is:

$$e_2 = \frac{B_1}{N_1 - Z_2} = \frac{\beta_1}{1 - z_2} \quad (12)$$

Since β_1 is known from EQUATION (11), one may calculate a value for e_2 by EQUATION (12) and compare it with a direct measurement. Conversely, if e_2 is known, one may calculate β_1 from either EQUATION (11) or (12) and, in subsequent calculations, use the value which is deemed the more precise.

The average chain length of LD₂ is obviously $\frac{1}{2}e_2$.

The fraction of glucoses split from LD₂ to form LD₂(g) is

$$X_2 = \frac{q''_0}{N_1 - Z_2} = \frac{\kappa''_0}{1 - z_2} \quad (13)$$

where

$$q''_0 = \sum q_{2n} + q_{20}$$

and

$$\kappa''_0 = \frac{q''_0}{N_1}$$

The fraction of Q-chains in the second tier is

$$f_2 = \frac{q''_0}{B_1} = \frac{\kappa''_0}{\beta_1} = \frac{X_2}{e_2} \quad (14)$$

The calculation of the average chain length of the second tier is complicated by the fact that the residues of the L-chains of the first tier contribute to the

value of Z_2 and must be subtracted for the calculation. There is, also, the possibility of a short L-chain of the first tier being connected to a short L-chain of the second tier so that their total length is five glucoses or less. These units would not be included in Z_2 . In the following, this possibility is neglected and the total residue of the L-chains in the first tier is subtracted from Z_2 . Furthermore, the equations for the application of the assumption of Case 1 to one tier and of Case 2 to the other tier will be omitted.

Case 1: If all chain lengths are (a) greater than five or (b) equal to or less than five

$$Z_2 = \sum nq_{2n} + \sum_{n=5}^{\infty} (n-5)l_{2n} + 5 \sum l_{1n} \quad \text{for } n > 5$$

$$Z_2 = \sum nq_{2n} + \bar{n}_1 \sum l_{1n} \quad \text{for } n \leq 5$$

and

$$\begin{aligned} \bar{n}_2 &= \frac{\sum nq_{2n} + \sum nl_{2n}}{\sum q_{2n} + \sum l_{2n}} = \frac{Z_2}{B_1} + 5 \frac{\sum l_{2n}}{B_1} - 5 \frac{B}{B_1} \cdot \frac{\sum l_{1n}}{B} \\ &= \frac{Z_2}{\beta_1} - 5f_2 \quad \text{for } n > 5 \quad (15a) \end{aligned}$$

since from EQUATIONS (5) and (11) it follows that

$$\frac{B}{B_1} = \frac{\kappa'_0}{f_1(\beta - \kappa'_0)} = \frac{1}{1 - f_1}$$

Also

$$\bar{n}_2 = \frac{Z_2}{\beta_1 f_2} - \frac{\bar{n}_1}{f_2} \quad \text{for } n \leq 5 \quad (15b)$$

If, as before, one includes the branch glucoses of the Q-chains in the average

$$\bar{n}_2' = \bar{n}_2 + f_2 \quad \text{for } n > 5 \quad (16a)$$

$$\bar{n}_2' = \bar{n}_2 + 1 \quad \text{for } n \leq 5 \quad (16b)$$

Case 2: For the case of random distribution of chain lengths, one has

$$\begin{aligned} Z_2 &= \sum nq_{2n} + \sum_{n=5}^{\infty} (n-5)l_{2n} + 5 \sum_{n=5}^{\infty} l_{1n} + \sum_{n=1}^4 nl_{1n} \\ &= \sum nq_{2n} + \sum (n-5)l_{2n} + \sum_{n=1}^5 (5-n)l_{2n} + 5 \sum l_{1n} - \sum_{n=1}^5 (5-n)l_{1n} \end{aligned}$$

The average chain length in the second tier is

$$\begin{aligned} \bar{n}_2'' &= \frac{Z_2}{B_1} + 5 \frac{\sum l_{2n}}{B_1} - R_2 \frac{\sum l_{2n}}{B_1} - 5 \frac{B}{B_1} \frac{\sum l_{1n}}{B} + R_1 \frac{B}{B_1} \frac{\sum l_{1n}}{B} \\ &= \frac{Z_2}{\beta_1} - 5f_2 - R_2(1 - f_2) + R_1 \quad (17) \end{aligned}$$

Including the branch glucose unit of the Q-chain makes the average chain length

$$\bar{n}_2''' = \bar{n}_2'' + f_2 \quad (18)$$

Setting

$$\sum q_{2n} + \sum l_{2n} = B_1$$

in the above equations, is equivalent to considering $LD_1(g)$ a new parent molecule without relation to the structure of the original molecule. The relation between the number of chains and the number of branch points discussed in the paragraphs immediately preceding EQUATION (1) is still applicable and B_1 is therefore equal to the number of outer chains of $LD_1(g)$. To examine the structure of $LD_1(g)$ with respect to the structure of the original molecule, it is necessary to pursue the question in more detail.

Since the $LD_1(g)$ molecule may be considered to be the interior of the original molecule which has $2B$ chains and its outer chains to be removed by the first successive treatments with phosphorylase and α -amylglucosidase, one would expect B chains and therefore $B/2$ branch points to be left in the $LD_1(g)$ molecule. However, this is true only for the case where $f_1 = 1/2$, e.g. the ideal Meyer model. The number of Q-chains in the first tier, q_0' , is also the number of branching glucoses removed by the first set of enzymatic actions and from EQUATION (5) is equal to $f_1 B$. The number of branches remaining in $LD_1(g)$ is $(1 - f_1)B$ and can be equal to $B/2$ only if $f_1 = 1/2$.

In all models, each branch point leads to one Q-chain and one L-chain, hence the total number of Q-chains must *always* equal the total number of L-chains. Now, if $f_1 > 1/2$ and one destroys more Q-chains than L-chains by the action of phosphorylase, then the subsequent action of α -amylglucosidase will destroy a compensating number of L-chains in the interior of the molecule, which is obviously equal to:

$$f_1 B - (1 - f_1)B = (2f_1 - 1)B$$

This destruction of interior L-chains does not involve degradation but simply the removal of a branch point between two other branch points and the corresponding lengthening of a chain. Therefore, one may calculate two average chain lengths for $LD_1(g)$: (a) on the basis of the dextrin molecule itself, which gives

$$\bar{n} = \frac{N_1}{2B_1} = \frac{1}{2\beta_1} \quad (19)$$

since there are $2B_1$ chains in the molecule; and (b) on the basis of the dextrin as the interior of the parent molecule, which gives

$$\bar{n} = \frac{N_1}{B} = \frac{1 - f_1}{\beta_1} \quad (20)$$

On the other hand, if $f_1 < 1/2$, more L-chains than Q-chains in the first tier are destroyed by phosphorylase. Subsequent action by α -amylglucosidase

again removes a number of branch points equal to

$$q_0' = f_1 B$$

but does not destroy a compensating number of Q-chains in the interior of the molecule. This dilemma is circumvented if one will consider the excess of L-chains in the first tier as not being destroyed but as being reduced to zero length which (neglecting the residues of five glucose units), in fact, they are. The number of such residues is

$$(1 - f_1)B - f_1 B = (1 - 2f_1)B$$

The average chain length for LD₁(g) is (a) on the basis of the dextrin itself (including the L-chains of zero length)

$$\bar{n} = \frac{N_1}{2B_1} = \frac{1}{2\beta_1} \quad (21)$$

and (b) on the basis of the dextrin as the interior of the parent molecule,

$$\bar{n} = \frac{N_1}{B} = \frac{1 - f_1}{\beta_1} \quad (22)$$

in fact, the same equations found for the case of $f_1 > \frac{1}{2}$.

It should be noted that one need not assume the ideal Meyer model pictured in FIGURE 3 as the only example for which $f_1 = \frac{1}{2}$. Another model is that obtained by considering the Haworth model and the Staudinger model attached at points A. One will note that, for each L-chain destroyed and a remaining chain lengthened by the removal of an interior branch point on the Staudinger side, there is an L-chain reduced to zero length on the Haworth side. The average chain length would, therefore, be the same as that obtained for the ideal Meyer model.

One may extend the analysis to the next residue, namely, LD₂(g). In this case, the molecule may be considered as an independent entity, as a derivative of its parent, LD₁(g), or as a derivative of its grandparent, the original molecule of glycogen. As an independent entity, one has for the average chain length,

$$\bar{n} = \frac{N_2}{2B_2} = \frac{1}{2\beta_2} \quad (23)$$

and, as a derivative of LD₁(g),

$$\bar{n} = \frac{N_2}{B_1} = \frac{1 - f_2}{\beta_2} \quad (24)$$

If one considers LD₂(g) as a derivative of the original molecule, one must take into account that there were originally $B/2$ chains in this section of the molecule, so that

$$\bar{n} = \frac{2N_2}{B} = \frac{2(1 - f_1)(1 - f_2)}{\beta_2}$$

It can be seen that, for the case of the ideal Meyer model in which $f = \frac{1}{2}$ in all tiers, the three average chain lengths become identical. The extension of the discussion to lower residual dextrans is obvious.

Unfortunately, one cannot, at the present time, tell how far in the interior of the molecule the imperfections arising from $f \approx \frac{1}{2}$ lie. It is, therefore, not possible to correlate exactly the average chain lengths of the individual tiers as they are uncovered by the action of the enzymes and the average chain lengths of the residual limit dextrans. However, the calculation of the f -factors for the successive tiers, the average chain lengths of the tiers, and the average chain lengths of the interiors enables one to construct models which represent our knowledge of the materials at the present time.

In TABLE 1, the f -values and the various averages of chain lengths calculated from the data of Larner, Illingworth, Cori and Cori is assembled. f_1 and f_2

TABLE 1

	f_1	f_2	Average chain lengths							
			First tier	Second tier	Residues					
					Original	LD ₁ (g)		LD ₂ (g)		
						<i>Per se</i>	Based on original	<i>Per se</i>	Based on LD ₁ (g)	Based on original
Rabbit liver glycogen	0.24	0.25	8.6	2.2	7.4	5.8	8.9	5.7	8.6	13.0
Rabbit muscle glycogen	0.48	0.39	7.6	5.3	7.4	8.2	8.6	7.6	9.3	9.7
Wheat amylopectin	0.63	0.32	10.4	8.2	9.3	10.4	7.7	7.4	10.0	7.4
Corn amylopectin	0.52	0.53	15.5	5.4	12.2	9.5	9.2	11.6	10.8	10.4

are calculated from EQUATIONS (5) and (14) respectively. The average chain lengths of the first and second tiers are calculated from EQUATIONS (10) and (18) respectively, and therefore include the first glucose unit of a Q-chain in the average. The average chain length of the original molecule is calculated from EQUATION (1), of LD₁(g) from EQUATIONS (21) and (22), and of LD₂(g) from EQUATIONS (23), (24) and (25).

In the case of the rabbit liver glycogen, the values of f are about 0.25, which indicates a deficiency of Q-chains, which is characteristic of the Haworth structure (FIGURE 3). More precisely, one should say that the structure lies about half way between the Haworth structure and the ideal Meyer structure. The rabbit muscle glycogen has a first tier, which is almost ideal, and a second tier with a small deficiency of Q-chains. Wheat amylopectin, with longer chains, has an excess of Q-chains in the first tier and a deficiency in the second tier. Corn amylopectin is almost ideal in the first two tiers and has a much larger chain length in the first tier than in the second.

With the use of this new method, one can expect to be able to characterize

amylopectins and glycogens from various sources more precisely and get a step closer to the solution of the problems of the biosynthesis of these polysaccharides.

The author is indebted to the Corn Industries Research Foundation for the support of this work.

References

1. ILLINGWORTH, B., J. LARNER, & G. T. CORI. 1952. J. Biol. Chem. **199**: 631.
2. LARNER, J., B. ILLINGWORTH, G. T. CORI, & C. F. CORI. 1952. J. Biol. Chem. **199**: 641.
3. STAUDINGER, H. & H. EILERS. 1936. Ber. **69**: 819.
4. STAUDINGER, H. & E. HUSEMANN. 1937. Ann. **527**: 195; 1938. Ber. **71**: 1057.
5. HAWORTH, W. N., E. L. HIRST, & F. A. ISHERWOOD. 1937. J. Chem. Soc. 577.
6. HAWORTH, W. N. 1939. Chem. and Ind. **17**: 917.
7. MEYER, K. H. & P. BERNFELD. 1940. Helv. Chim. Acta. **23**: 875.
8. MEYER, K. H. 1942. Advances in Colloid Science. **1**: 143.
9. SILLÉN, L. G. & K. MYRBÄCK. 1943. Svensk. Kem. Tids. **55**: 294.
10. PERCIVAL, E. G. V. 1950. Structural Carbohydrate Chemistry. Prentice-Hall. New York.
11. FLORY, P. J. 1941. J. Am. Chem. Soc. **63**: 3083, 3091, 3096.
12. STOCKMAYER, W. H. 1943. J. Chem. Phys. **11**: 45.
13. KERR, R. W. 1950. Chemistry and Industry of Starch. Academic Press. New York.
14. PERCIVAL, E. G. V. 1950. Structural Carbohydrate Chemistry. Prentice-Hall. New York.
15. WHISTLER, R. L. & C. L. SMART. 1953. Polysaccharide Chemistry. Academic Press. New York.
16. CORI, G. T. & J. LARNER. 1950. Federation Proc. **9**: 163.
17. CORI, G. T. & J. LARNER. 1951. J. Biol. Chem. **188**: 17.
18. HESTRIN, S. 1949. J. Biol. Chem. **179**: 943.

BRANCHING IN POLYETHYLENE

By Frank M. Rugg, Joseph J. Smith, and Lloyd H. Wartman*

Research Department, Bakelite Company, Division of Union Carbide and Carbon Corporation, Bloomfield, N. J.

Introduction

The principal purpose of this paper is to present the current status, as viewed by the authors, of our knowledge of branching in polyethylene and the effects of branching on its properties. Another purpose is to present some speculative material, and some challenging observations, in an attempt to stimulate, in some measure, future work on the structure and chemistry of polyethylene. In endeavoring to achieve these aims, the authors have drawn heavily upon their own work and liberally from the literature, particularly the published results of R. B. Richards and his collaborators.

Polyethylene resins are made by polymerizing ethylene at elevated temperatures and high pressures.^{1, 2} The polymer molecules formed under these conditions are branched hydrocarbon chains^{3, 4, 5, 6} and their average molecular size varies from approximately 50 carbon atoms per molecule, for the greasy products, to more than 1000 carbon atoms per molecule for rigid resins. The degree of branching in polyethylene has been shown to play an important role in determining the properties of the resin.⁷ In fact, it is now generally recognized that degree of branching and molecular weight are the most important molecular variables in polyethylene resins.

In this paper, degree of branching is defined as the number of branches per 100 carbon atoms, and the number of branches per molecule is defined as the number of $-\text{CH}_3$ groups per molecule more than two. Although some chains and branches are terminated by vinyl groups ($-\text{CH}=\text{CH}_2$), the concentration of these is very small compared to the concentration of methyl groups. Side chain methylene groups ($\text{RR}'\text{C}=\text{CH}_2$) may be regarded as short branches but, as such, represent not more than 15 per cent, and generally a much smaller proportion, of the total number of branches. As a result, this configuration is not considered significant for the purposes of this paper.

Determination of Branching

The number of branches per 100 carbon atoms can be calculated from the methyl content and number average molecular weight of a polyethylene resin. This is illustrated by the following equation which has been employed by the authors to calculate branching:

$$\text{Branches/100 carbons} = \frac{14}{15} \left[\% \text{CH}_3 - \frac{3000}{\text{no. av. mol. wt.}} \right]$$

In deriving this equation, it was assumed that a $-\text{CH}_3$ group is present at the end of each branch and at each chain end. According to this assumption, the

* Present address: Bakelite Company, Development Laboratories, Bound Brook, N. J.

number of methyl groups per molecule more than two corresponds to the number of branches per molecule.

The branching data reported in the literature thus far for polyethylene have been obtained from an infrared spectrophotometric determination of methyl content. Molecular weight values for the resins have been determined by an ebulliometric technique or by an osmotic pressure method.

Determination of $-\text{CH}_3$ content. In the spectrum of polyethylene, the absorptions at 3.38 microns³ and 7.25 microns^{4, 5} are due to methyl groups. For solid polyethylene films, the extent of absorption at these band centers, particularly the latter, is dependent on the degree of crystallinity of the sample. Consequently, for most accurate results, measurements should be made on resins in the molten state or in solution. Probably the most accurate technique now available involves the use of a high dispersion spectrophotometer (LiF prism or grating) to measure the intensity of absorption at 3.38 microns by a hot solution of the resin in a non-absorbing solvent.

Typical spectra for hot CCl_4 solutions of polyethylene resins obtained by use of a 3600 line per inch grating (second order) are shown in FIGURE 1. The broken lines show the effective incident radiant energy curves used in applying the Beer-Lambert Law to the determination of $-\text{CH}_3$ content at 3.38 microns and $-\text{CH}_2-$ content at 3.502 microns.³ Calibration constants, *i.e.* absorptivities, at these wavelengths were obtained from the spectra of hot CCl_4 solutions of known concentrations of *n*-hexadecane and *n*-octadecane. The $-\text{CH}_3$ and $-\text{CH}_2-$ values obtained are shown in TABLE 1 for a series of Bakelite resins covering the range of 880 to 9,100 in number average molecular weight (1,000–21,000 viscosity average molecular weight). Resins of higher molecular weight were not sufficiently soluble in hot CCl_4 to give acceptable spectra.

In TABLE 1, the total of the $-\text{CH}_3$ and $-\text{CH}_2-$ values accounts for 99 per cent of the resin in the case of the highest molecular weight resin, but this total decreases as molecular weight decreases. This can be explained, in part, by

the higher concentration of $-\text{CH}$ (branching) and $\text{C}=\text{C}$ groups found as molecular weight decreases. For example, the sum for DXL-1 of the $-\text{CH}_3$ (10.5 per cent) and $-\text{CH}_2-$ (65 per cent) values is only 79.5 per cent. Adding the $\text{C}=\text{C}$ content (3 per cent) found by iodination and the $-\text{CH}$ content (6 per cent), calculated from the branching data, brings the total for this resin to almost 90 per cent.

Determination of molecular weight. Ray,⁸ using a boiling point elevation technique, and Harris,⁹ using an osmotic pressure method, have made number average molecular weight measurements on several grades of polyethylene resins manufactured by the Imperial Chemical Industries. Their results, given in TABLE 2, illustrate the general lack of agreement between molecular weight measurements on polyethylene by these two methods.

Some number average molecular weight measurements on some Bakelite polyethylene resins are given in TABLE 3. The values by boiling point elevation, with one exception, were obtained by Quick¹⁰ using a modified Menzies-

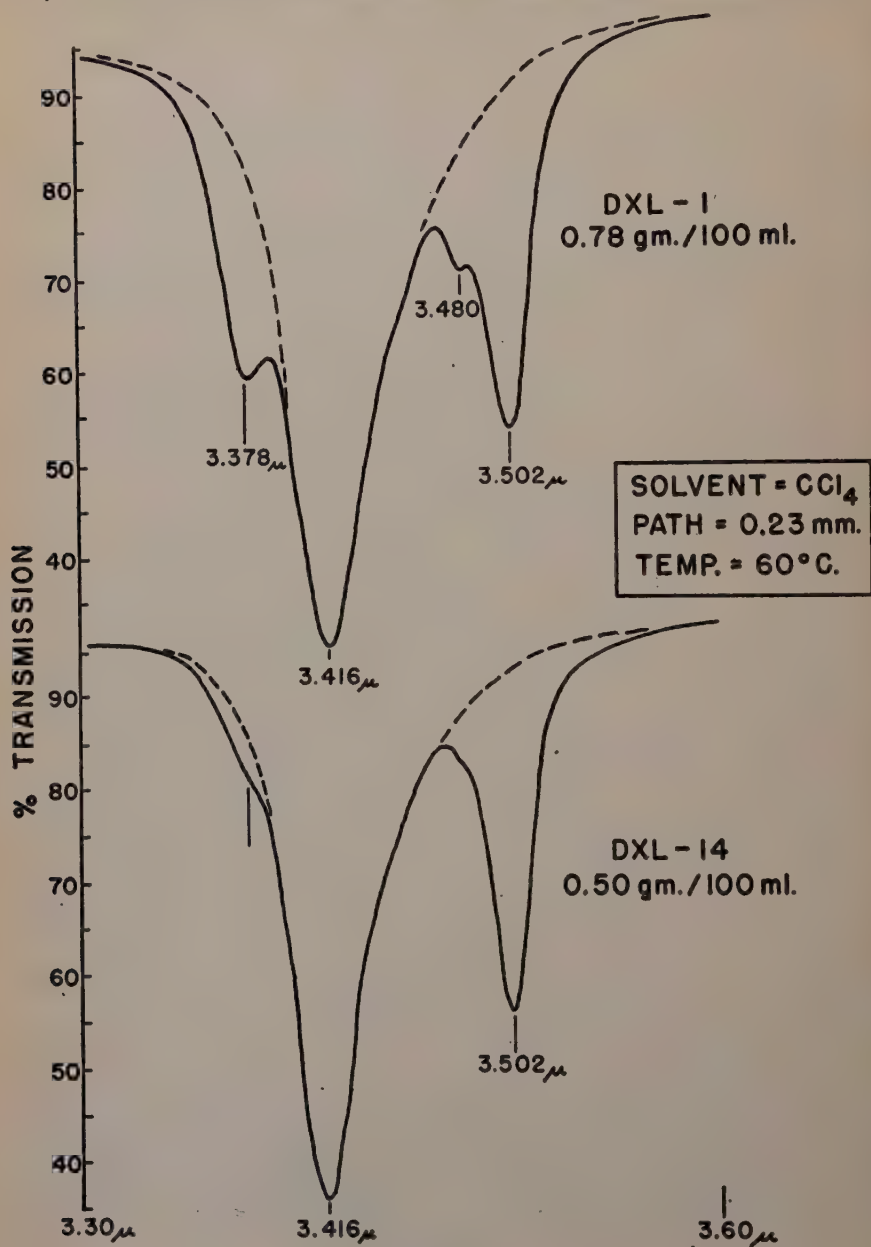


FIGURE 1.

Wright ebulliometer developed by Hill and Brown.¹¹ The value of 9,100 for DYNH was determined by Morawetz.¹² The number given in the resin designation in TABLE 3 indicates the viscosity molecular weight value,¹³ *e.g.* 10,000 for DYJT (10).

TABLE 1
STRUCTURAL DATA ON A SERIES OF POLYETHYLENE RESINS

Resin	No. av. mol. wt.	% $-\text{CH}_2-$ (3.50 μ)	% $-\text{CH}_2-$ (3.38 μ)	Branches per 100 carbons
DXL-1	880	69	10.5	6.6
DYDT	3300	79	6.1	4.8
DXL-6	4000	86	5.3	4.2
DYJT	5700	85	4.3	3.5
DYLT	6700	89	3.4	2.8
DXL-14	—	93	2.6	—
DYNH	9100	97	1.8	1.3

TABLE 2

Polyethylene resin (ICI)	Number average molecular weight	
	Boiling point elevation (Ray)	Osmotic pressure (Harris)
<i>Grade</i>		
200	10,000	19,000
20	12,000	24,000
7	14,300	28,000
2	34,000	32,000

TABLE 3

Polyethylene resin (U.C.C.)	Number average molecular weight		
	Boiling point elevation (Hill & Brown)	Infrared $\text{C}=\text{C}$ content	Osmotic pressure (Harris)
DXL-1	880	860	—
DYJT (10)	5,700	9,600	—
DXL-14	6,700	14,000	—
DYNH (21)	9,100*	27,000	26,000

* Morawetz.

The number average molecular weight values given in TABLE 1 were obtained by boiling point elevation. FIGURE 2 is a plot of degree of branching versus number average molecular weight for the resins of TABLE 1. This graph must not be interpreted to mean that an increase in molecular weight automatically means a decrease in degree of branching. The degree of branching depends on the conditions under which the resins are made.

The number average molecular weight values in the "Infrared $\text{C}=\text{C}$ Content" column, TABLE 3, require some explanation. These values are based on two assumptions: (1) The total double bond content in polyethylene resins can be measured by infrared; (2) there is one double bond per molecule.

That the first assumption is reasonable for these resins has been shown by Rugg, Smith, and Wartman,¹³ and the change in degree of absorption by the infrared band employed, with change in molecular weight, is illustrated in FIGURE 3. The second assumption is open to question, but it is particularly interesting that, for the lowest molecular weight resin (TABLE 3) there is excellent agreement with the ebulliometric value and, for the highest molecular weight resin, there is excellent agreement with the osmotic pressure value by Harris.⁹

The data of TABLES 2 and 3 clearly indicate a need for the development of more accurate methods or the refinement of present methods of molecular weight measurement.

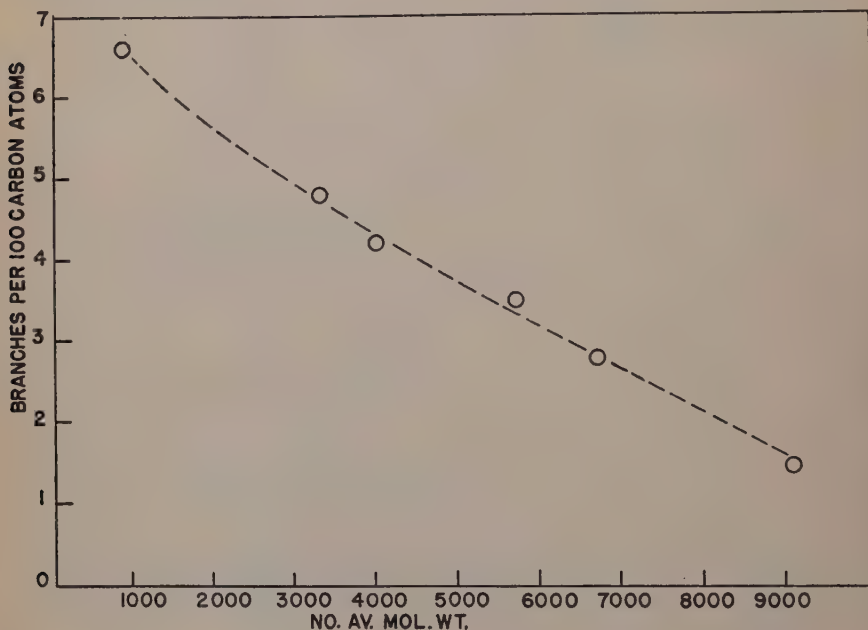


FIGURE 2.

Importance of Crystallinity in Polyethylene

X-ray analyses by Bunn and Alcock¹⁴ revealed the presence of crystalline and amorphous regions in polyethylene resins, and it has been subsequently shown that crystalline content has a profound effect on several of the mechanical properties of the resin.

Hunter and Oakes¹⁵ determined the crystalline contents of polyethylene resins by measuring the density of the ethyl alcohol-water mixture in which the sample would remain suspended, neither sinking nor floating. Crystalline content has also been determined from heat content data by Raine, Richards, and Ryder,¹⁶ and from heat of combustion data by Parks and Mosley.¹⁷ A comparison of the results of these three methods on similar samples gave a crystalline content of 60 ± 10 per cent (TABLE 4). Krimm and Tobolsky¹⁸

showed that the crystalline content (40 per cent) estimated from coherent amorphous scattering of X-rays for a particular sample was in agreement with the value calculated from density data.

An estimate of crystalline content can also be obtained from the intensity

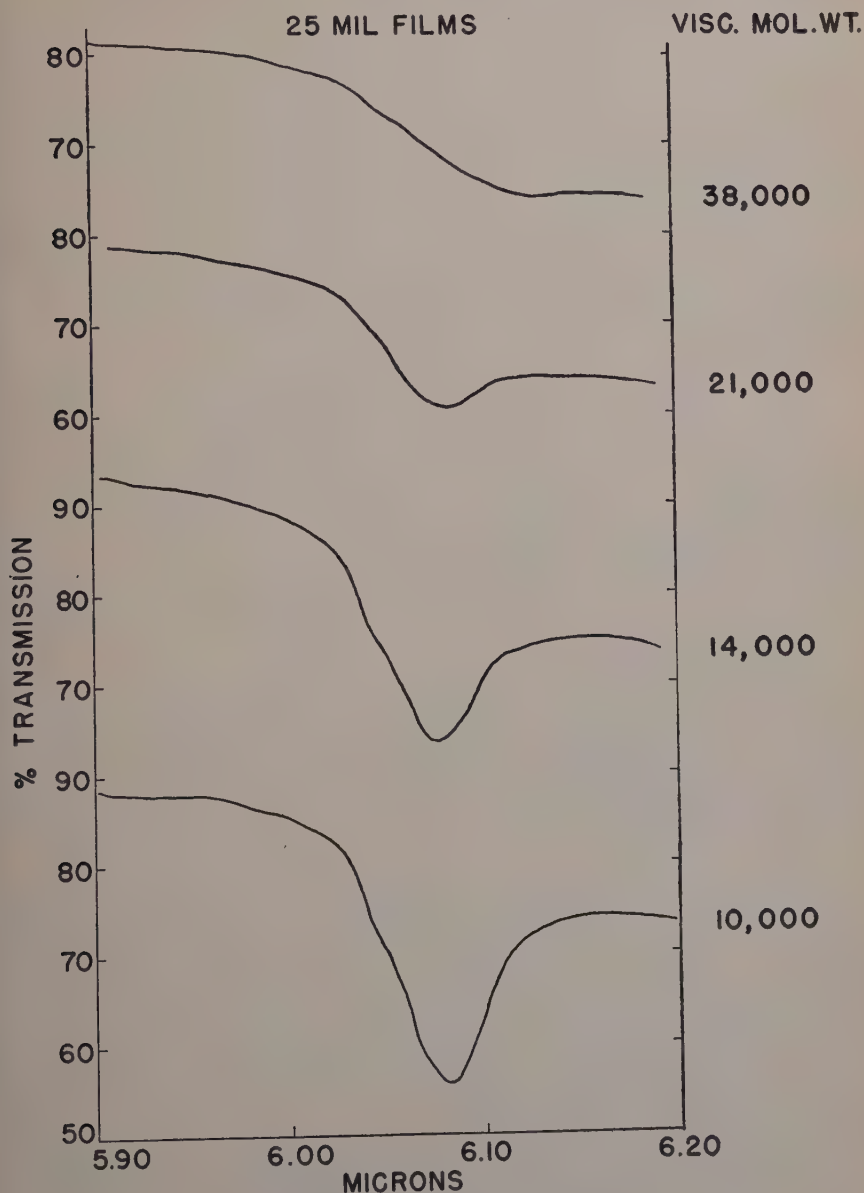


FIGURE 3. Variation in C=C absorption.

of the absorption band at 13.7 microns in the infrared spectrum of a thin, solid film of a polyethylene sample.⁷ FIGURE 4 shows that this absorption completely disappears when the film is melted.

Variations in crystalline content and average molecular weight are largely responsible for the differences observed in the mechanical properties of various polyethylene resins. The effect of crystalline content on properties is illustrated in TABLE 5. Although both resins have the same number average molecular weight, the one with the higher crystalline content, *i.e.* higher density, is a hard brittle wax while the one with the lower crystalline content is a stiff grease. Richards⁷ has extended this type of study over a wide molecular weight range as is shown in FIGURE 5. The results summarized in this figure point up the fact that, for a given molecular weight, the higher the crystalline content the harder the resin.

Richards⁷ has concluded that those properties which concern slight movements of portions of the resin relative to each other are particularly sensitive to crystalline content and are only slightly dependent on average molecular

TABLE 4
ESTIMATED CRYSTALLIZATION, POLYETHYLENE AT 25°C

Investigators	Method	Percentage crystallized
Parks and Mosley	Heat of combustion	49 to 52
Hunter and Oakes	Density	55
Raine, Richards and Ryder	Computation-enthalpy data	74
Raine, Richards and Ryder	Extrapolation-enthalpy data	61

"Best" estimate = $60 \pm 10\%$

(From Parks and Mosley, *J. Chem. Phys.* **17**: 693, 1949).

weight. These properties include melting point, softening point under low load, Young's modulus in tension, bending modulus, yield point, and surface hardness. Such properties as tensile strength, low temperature brittle point and tear resistance are more dependent on average molecular weight, although crystalline content is also a factor.

Dependence of Crystallinity on Branching

Fractions of varying molecular weight isolated from a given polyethylene resin have been found to have essentially the same structure, including degree of branching. In such a series of fractions, crystalline content is observed to increase slightly with decreasing molecular weight.⁷ Furthermore, the crystalline content of the fraction nearest in molecular weight to the total resin is only slightly greater than the crystalline content of the total resin. These results show that the effect of average molecular weight and molecular weight distribution on crystallinity is small.

The effect of degree of branching on crystallinity is much more pronounced, as is illustrated in TABLE 6. These resins have essentially the same average molecular weight (25,000). The only significant structural variable is found

DYNH - 21,000
(1-2 MIL FILMS)

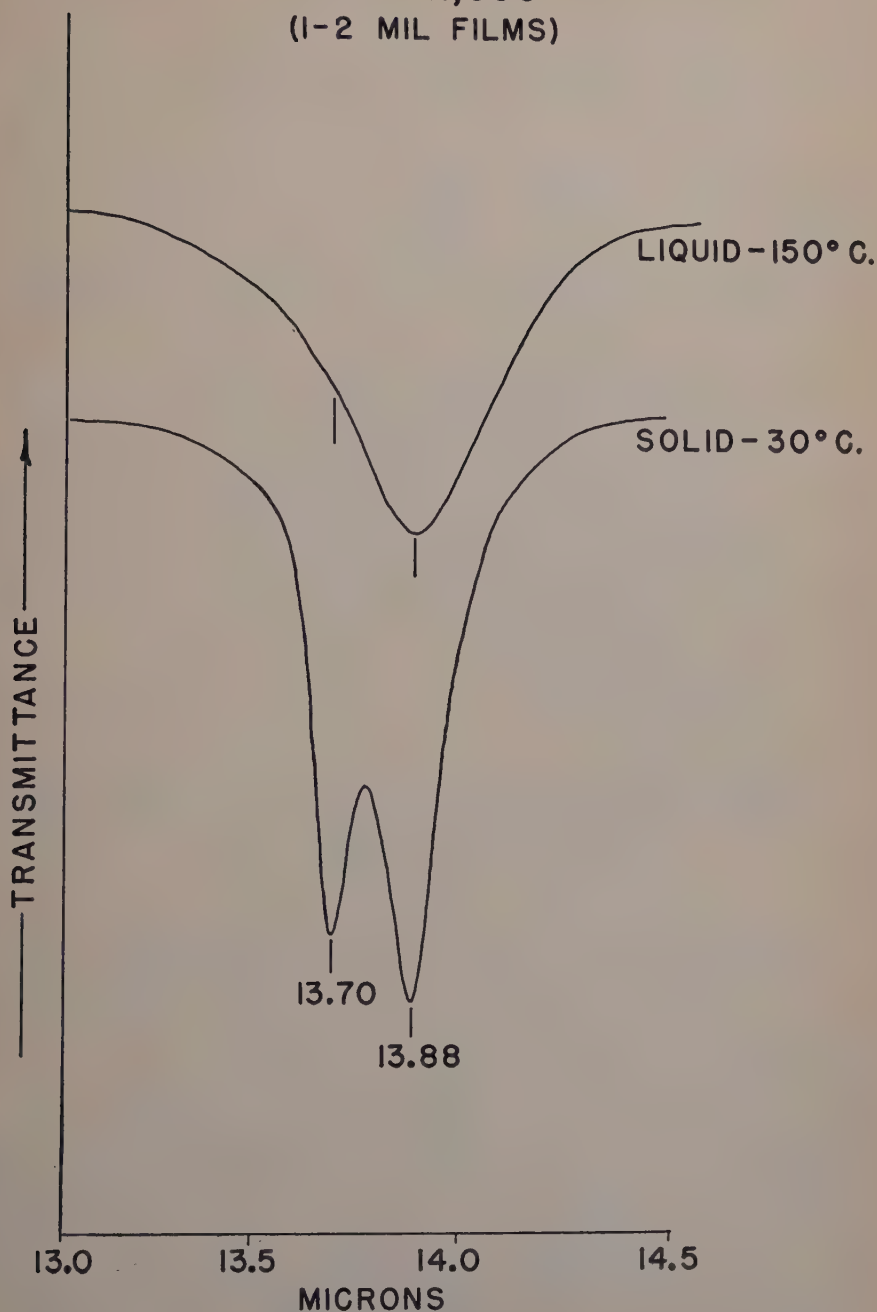


FIGURE 4.

in the fact that the polymethylene molecules are unbranched¹⁹ while the polyethylene molecules contain approximately three branches per 100 carbon

TABLE 5
EFFECT OF CRYSTALLINE CONTENT ON RESIN PROPERTIES

Sample	A	B
Molecular weight	2500	2500
Density g/cc	0.935	0.895
Appearance	Hard wax	Stiff grease
Melting point °C	120	95
Softening point °C	85	45

(From Richards, J. Appl. Chem. 1: 371, 1951).

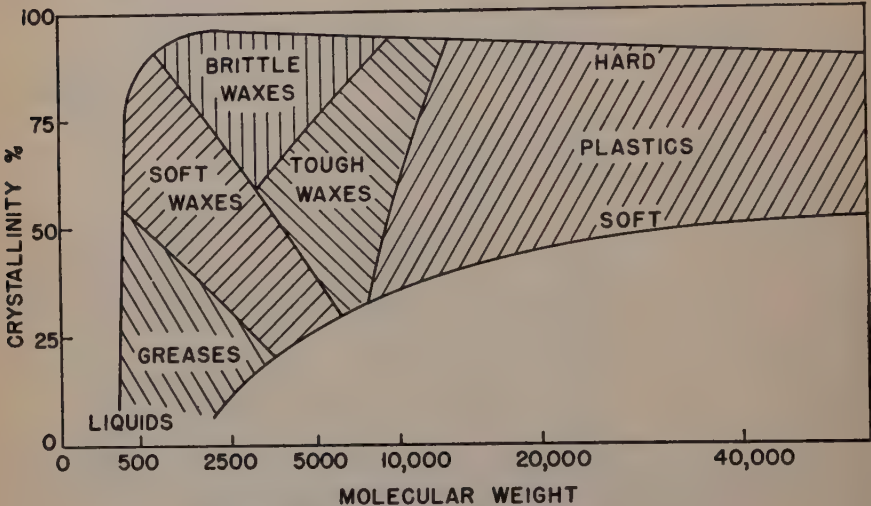


FIGURE 5. (From Richards, 1951, J. Appl. Chem. 1: 371.)

TABLE 6
EFFECT OF DEGREE OF BRANCHING ON CRYSTALLINE CONTENT

Sample	Polymethylene	Polyethylene
Chain branching (CH ₃ per 100 CH ₂ groups)	nil	3
Density, g/cc	0.98	0.92
Crystallinity at 20°C	ca.95%	ca.60%
Melting point, °C	130	110
Brittleness	Brittle at 20°C	Flexible at -40°C
Extensibility	<10%	Cold drawn to 400%

(From Richards, J. Appl. Chem. 1: 371, 1951).

atoms. This structural difference results in a much higher crystalline content for the polymethylene resin (95 per cent) than is found in the polyethylene sample (60 per cent).

FIGURE 6 shows the 14 micron region spectra of a series of Bakelite resins (TABLE 1) varying from a soft grease (A) to a very hard plastic (E). That the crystalline content in this series increases from A (lowest) to E (highest) is shown both by the increasing intensity at 13.7 microns and by the increasing density values. The increase in degree of crystallinity from resin A to resin E

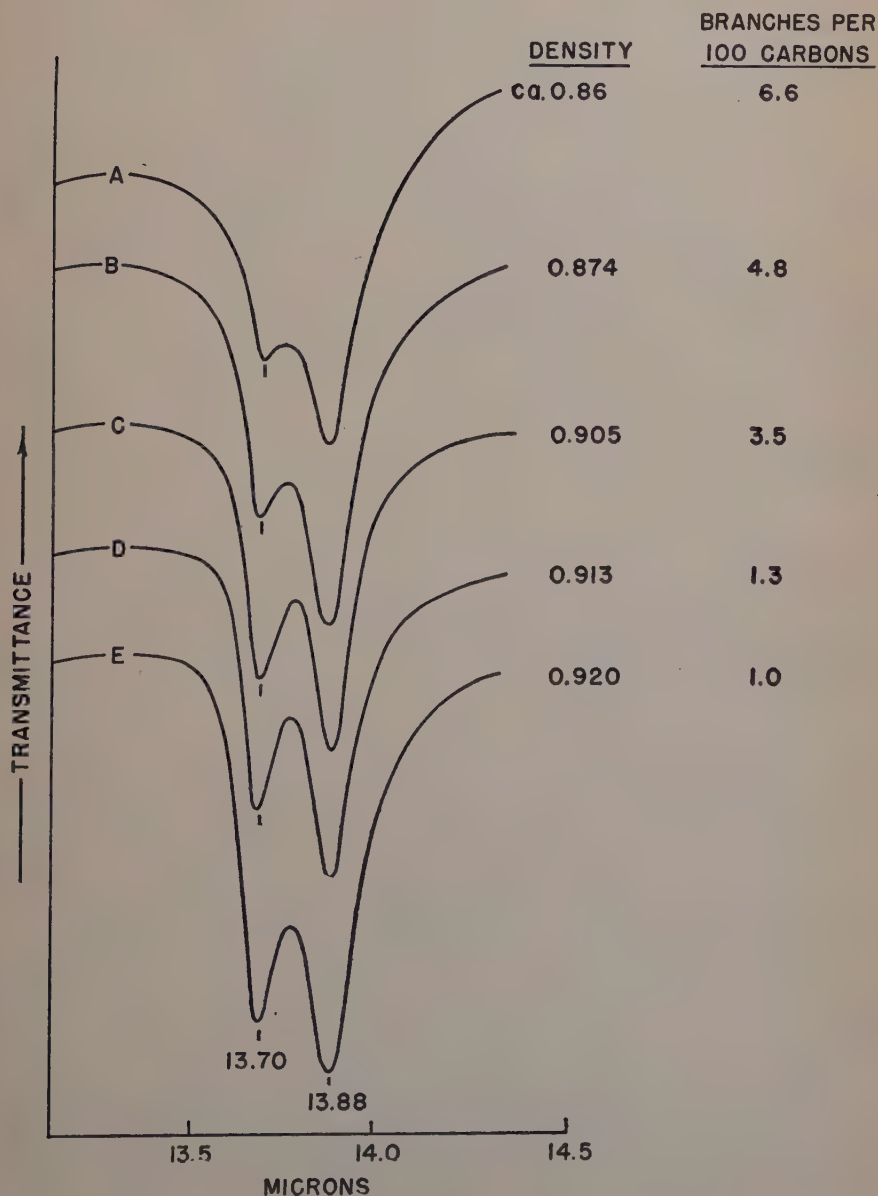


FIGURE 6.

is almost certainly a result of the fact that degree of branching decreases from resin A to resin E.

0.7 MIL FILM OF STRETCHED RUBBER

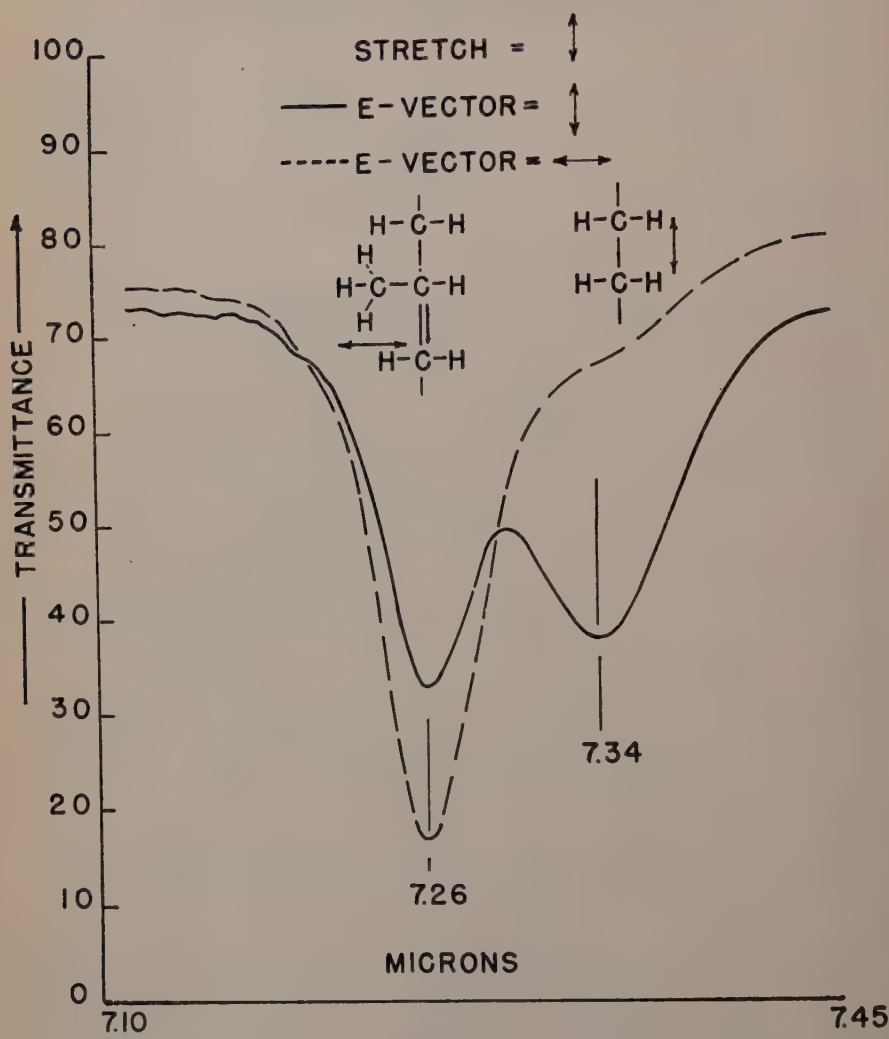


FIGURE 7.

Length of Branches

Observations at 7.3 microns. In FIGURE 7 are given spectra of a 1 mil film of vulcanized gum latex natural rubber stretched by a factor of at least 6. It is generally accepted that stretching rubber to such an extent produces a high degree of orientation of the molecules parallel to the direction of stretch.

Therefore, it is not surprising that radiation polarized at right angles (E-vector vibrating at right angles) to the direction of stretch gives a spectrum different from that obtained with the radiation polarized parallel (E-vector vibrating parallel) to the direction of stretch.

The spectra of FIGURE 7 show that the 7.34 micron band arises from a vibration parallel to the long chain axis and that the 7.26 micron band arises from a vibration at right angles to the long chain axis. This observation has previously been made by Sutherland and Jones.²⁰ The 7.34 micron band involves methylene groups and the 7.26 micron band is characteristic of methyl groups. It is now generally agreed that the 7.26 micron band arises from the symmetrical deformation vibration of the methyl group, a vibration involving a dipole change parallel to the bond to the adjacent carbon. Accordingly, it is not surprising that for rubber the 7.26 micron band is deeper with the E-vector at right angles to the direction of stretch than with the E-vector parallel to the direction of stretch.

These spectra show that methyl groups are preferentially oriented in stretched rubber. Similarly, one might expect to observe orientation of methyl groups in highly stretched polyethylene. If the branches are predominantly long, and oriented parallel to the direction of stretch, the 7.25 micron band should be deeper with the E-vector parallel to the direction of stretch. Conversely, if the branches are very short, one might expect the 7.25 micron band to be deeper with the E-vector at right angles to the direction of stretch. The spectra of FIGURE 8 reveal, however, that the $-\text{CH}_3$ band is approximately equally intense for parallel and perpendicular radiation. This suggests that a substantial portion of the branches are short.

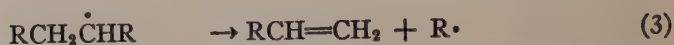
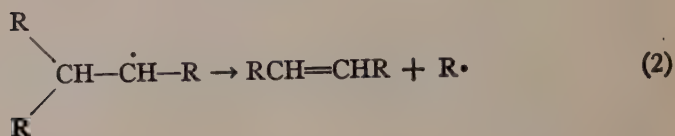
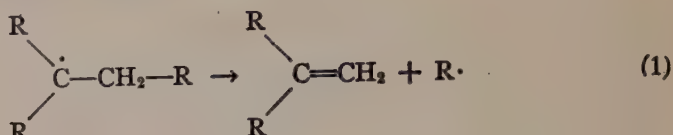
These findings are not in accord with Elliott, Ambrose, and Temple²¹ whose infrared results led them to conclude that the branches are sufficiently long to become oriented parallel to the direction of stretch. Because of the low resolution of their instrument, they were misled by the behavior of the adjacent 7.30 and 7.39 micron bands.

Observations at 13.0 microns. Smith²² has shown that ethyl branches in hydrocarbons absorb close to 13.0 microns. Linear hydrocarbons, such as octadecane and polymethylene,¹⁹ as well as hydrocarbons containing only methyl, propyl, or butyl branches, give little, or no, absorption at this wavelength. Hydrocarbon polymers, however, containing ethyl branches, such as: (1) that prepared by Buckley, Cross, and Ray¹⁹ from diazopropane; (2) hydrogenated polybutadiene (Hydropol, from Phillips Petroleum Company), give a pronounced absorption near 13.0 microns. Hydrocarbon polymers containing amyl branches also give an absorption in this region.³⁰

Polyethylene resins display a significant absorption band in this region of the spectrum, and the absorption is more intense in those resins having high degrees of branching. Of particular significance is the fact that polyethylene grease, having a high degree of branching and a methyl group content approximately the same as octadecane, gives a pronounced absorption at 13.0 microns while octadecane does not. These results clearly indicate that a substantial portion of the branches in polyethylene resins are ethyl and/or amyl branches.

Effect of Branching on Thermal Decomposition

The following depolymerization reactions, first suggested by Oakes and Richards,²³ are proposed as the principal decomposition processes by which polyethylene is degraded during pyrolysis.



In this thermal degradation process, it is assumed that the primary radicals formed generate more secondary and tertiary radicals by hydrogen extraction.

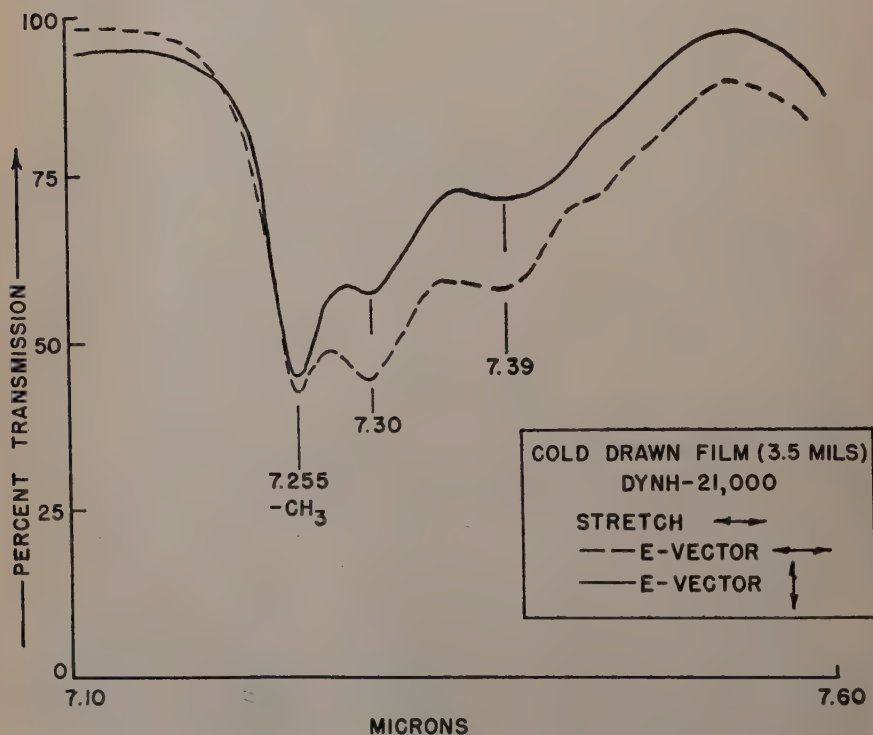


FIGURE 8.

These, in turn, depolymerize, thus propagating the process. As the removal of tertiary hydrogens requires less energy than the removal of secondary hydrogens, the generation of tertiary free radicals is favored unless other factors intervene, such as the depletion of tertiary carbons. Wall²⁴ has shown that only traces of ethylene are liberated during thermal decomposition of polyethylene. Consequently, no provision is made for its formation in the proposed thermal decomposition scheme.

Oakes and Richards²³ pyrolyzed two polyethylene resin samples at 330°C. for two hours and obtained the results shown in TABLE 7. The samples differed from each other in that one sample was more highly branched than the other. During this thermal treatment, more C—C bonds were broken in the resin

TABLE 7
PYROLYSIS: 2 HOURS AT 330°C

Sample	A	B
Chain branching	Low	High
C—C broken per g. ($\times 10^{-20}$)	0.38	0.64
Vinyl as % of total C=C	47	39

(Oakes & Richards, J. Chem. Soc. 2929, 1949).

TABLE 8
EFFECT OF DEGREE OF THERMAL DEGRADATION ON DOUBLE BOND COMPOSITION

Mol. wt.	Optical density		
	RCH=CH ₂ (11.0 μ)	RCH=CHR (10.35 μ)	RRC=CH ₂ (11.26 μ)
13,000 (original)	<0.1	<0.1	<0.1
5,000	0.25	0.17	0.17
1,100	0.40	0.22	0.24
700	0.52	0.27	0.28
500	0.90	0.27	0.30

(From: Oakes & Richards, J. Chem. Soc. 2929, 1949).

that was more highly branched and, in the two degraded resins the vinyl double bond content, expressed as per cent of total unsaturation, was less for the originally more highly branched resin. These results suggest that decomposition occurs preferentially at the branch points and that decomposition at branch points does not produce vinyl groups. These suggestions are consistent with the decomposition scheme proposed above.

TABLE 8 gives a series of optical density (absorbance) data²³ for each of three double bond bands on a resin thermally degraded to different extents. The concentration of each type double bond is proportional to the corresponding density values. The point to be emphasized is that the amount of RCH=CHR and RRC=CH₂ ceased to increase at a degree of degradation corresponding to a molecular weight of approximately 700 while the amount of RCH=CH₂ continued to increase with further degradation. As the "molecular weight" of the average length of straight chain segments in the original resin is pre-

sumed to be approximately 700, it would seem reasonable to suggest, as an explanation of this phenomenon, that at this degree of degradation most of the branch points had been destroyed. As a consequence, the reaction rates of reactions 1 and 2 approached zero while reaction 3 would continue unabated.

FIGURE 9 shows how the rate at which C—C bonds are broken drops off as decomposition increases. As the percentage of C—C bonds broken is less than 1.0 per cent, if all bonds were equally likely to break at a given tempera-

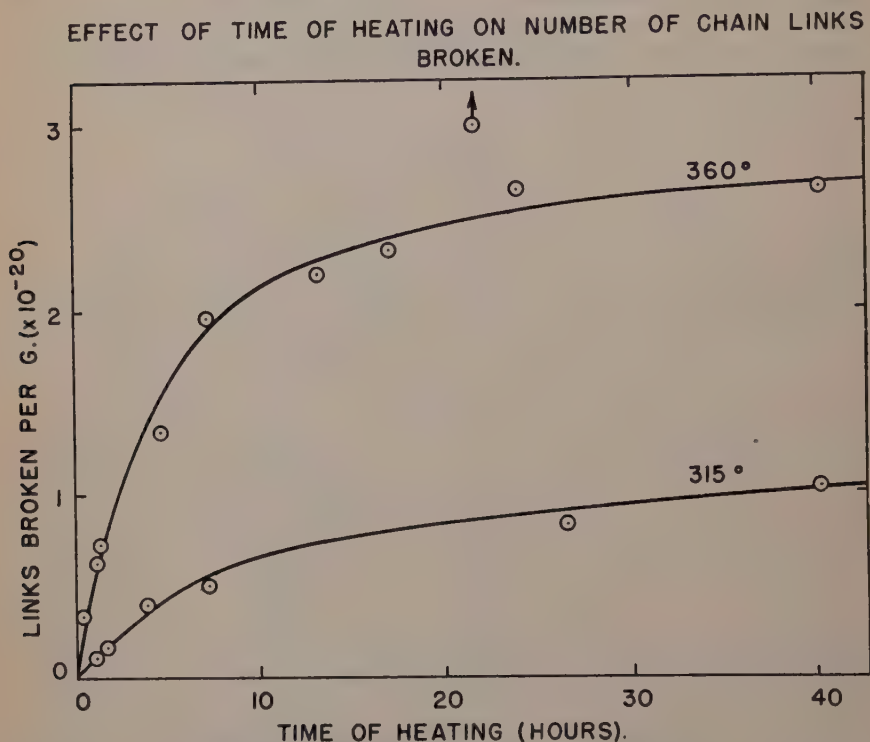


FIGURE 9. (From Oakes & Richards, 1949, J. Chem. Soc.: 2929.)

ture, these plots would have been straight lines. This decrease in decomposition rate with time suggests the presence of weak links in polyethylene. Another fact which suggests weak links in polyethylene is that polyethylene is unstable at temperatures as low as 290°C., while *n*-hexadecane in the absence of a catalyst is stable at 390°C.

At 360°C., more links are broken than at 315°C. (FIGURE 9). This might suggest varying degrees of weakness of links in polyethylene, but more likely it means that decomposition progresses by a chain mechanism and that at the higher temperature more decomposition or depolymerization occurs per weak link.

If thermal degradation does take place primarily at branch points, degraded

polyethylene should be less branched than the original resin. By thermal degradation, Brown and Reding²⁵ have reduced the molecular weight of a polyethylene resin from 24,000 to approximately 2,600. The data given in TABLE 9 show that the degraded product was less branched than the original resin. On the basis of degradation reactions 1 and 2, one would expect thermal degradation to reduce degree of branching.

The thermal degradation data presented in this section are consistent with, and can be explained by, the following statements which summarize the proposed thermal decomposition scheme for polyethylene: (1) Thermal decomposition is a chain process; (2) Initiation occurs at weak links; (3) Decomposition occurs primarily by the three depolymerization reactions presented above; and

TABLE 9
EFFECT OF PYROLYTIC DEGRADATION ON DEGREE OF BRANCHING

Mol. wt. (viscosity)	Density	Degree of branching
24,000	0.9167	1.3
2,600	0.9250	0.3

Brown & Reding—private communication.

TABLE 10
SOME PERTINENT POLYMERIZATION AND STRUCTURAL DATA FOR AN EXPERIMENTAL RESIN

Free radical/oxygen atom	1
% O ₂ in ethylene	0.0016
% conversion	16%
Ethylenes polymerized/free radical	5,720
No. av. molecular weight	20,000
Molecules/free radical	8
% methyl	1.8
Degree of branching	1.4
Branches/free radical	160

(4) Depolymerization is propagated preferentially through the points of branching.

How Branches Are Produced

In this section, a scheme of ethylene polymerization reactions is presented to account for the observed molecular weight, degree of branching, double bond content, and relative amounts of double bonds in polyethylene. As an illustration, an experimental resin was used and, except for double bond values, the pertinent data are summarized in TABLE 10.

It is assumed that each oxygen atom, in some way, generates only one free radical, and it is assumed that oxygen is the only significant source of free radicals—an assumption with reasonable support.

The ethylene used in making this experimental resin contained 16 parts of oxygen per million parts of ethylene by weight; the conversion was 16 per cent; and all the oxygen was consumed during this 16 per cent conversion.

From the first three values given in TABLE 10, the number of ethylene molecules polymerized during the average kinetic lifetime of one free radical was calculated to be 5,720. The number average molecular weight of 20,000 is a compromise value. Osmotic pressure values are higher and boiling point elevation values are lower. Fortunately, the validity of the proposed polymerization scheme is not dependent upon knowing the exact value of molecular weight. The methyl content was determined by infrared and the remaining values were calculated.

The proposed average kinetic life history of a free radical in producing this experimental resin is presented in TABLE 11. The standard free energy values are for room temperature. They were obtained either directly from Bryant²⁶ or estimated from handbook data.

TABLE 11
PROPOSED AVERAGE KINETIC LIFE HISTORY OF A FREE RADICAL

Reaction no.	Reaction	Units of reaction	ΔF° (kcal)
1	$R + \text{Oxygen} \rightarrow R\cdot$	1	
2	$R\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{RCH}_2\text{CH}_2\cdot$	5700	-12
3	$R\cdot + \text{RCH}_2\text{R} \rightarrow \text{RH} + \text{R}\dot{\text{C}}\text{HR}$	160	-6
4	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}-\text{CH}_3\text{R} \\ \diagup \\ \text{R} \end{array} \rightarrow \begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{R} \end{array} + \text{R}\cdot$	4	+19
5	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{CH}-\dot{\text{C}}\text{HR} \\ \diagup \\ \text{R} \end{array} \rightarrow \text{RCH}=\text{CHR} + \text{R}\cdot$	1.5	+16
6	$\text{R}\dot{\text{C}}\text{H}-\text{CH}_2\text{R} \rightarrow \text{RCH}=\text{CH}_2 + \text{R}\cdot$	1.5	+16
7	$\text{R}\cdot + \text{R}\cdot \rightarrow \text{RR}$	0.5	-59

By EQUATION 1, no suggestion as to how oxygen reacts to generate free radicals is intended. What R and R \cdot are is not known, but, presumably, what they are has no great bearing on the general picture conveyed by this scheme of reactions.

EQUATION 2 represents the propagation reaction, and EQUATION 3 represents chain transfer to a polymer molecule. Chain transfer is proposed as the process responsible for branching. By reaction 2, branches will, of course, grow out from the radicals formed by reaction 3.

In Bakelite's polyethylene resins, throughout the molecular weight range of 1000 to 38,000, the unsaturation is distributed approximately as follows: 60

per cent as side-chain methylene groups, $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{R} \end{array}$; 20 per cent as vinyl

groups, $\text{RCH}=\text{CH}_2$; and 20 per cent as internal double bonds, $\text{RCH}=\text{CHR}$. EQUATIONS 4, 5, and 6 are depolymerization reactions by which most of these

double bonds are presumed to form. The absolute and relative number of times each of these reactions occurs during the average kinetic lifetime of a free radical largely determines the number average molecular weight and the relative amounts of double bonds found in the resulting polymer.

Reactions 4, 5, and 6 are not favored thermodynamically, but entropy changes favor depolymerization and the higher the temperature the less unfavorable is ΔF° , *i.e.* the less unfavorable is depolymerization. Dainton and Ivin²⁷ have proposed and discussed the use of the equation,

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

where T is expressed in degrees Kelvin, for calculating the temperatures at which the free energy changes for polymerization reactions are zero. From Bryant's²⁶ ΔH° and entropy values, these temperatures have been calculated by means of this equation for reactions 4, 5, and 6. They fall in the range of 450–550°C. If one accepts the idea of the coexistence of polymerization and

TABLE 12
SOME OTHER REACTIONS OF INTEREST

Reaction no.	Reaction	ΔF° (kcal)
8	$\text{R}\dot{\text{C}}\text{HCH}_2\text{R} + \text{CH}_2=\text{CH}_2 \rightarrow \text{RCH}=\text{CHR} + \text{CH}_3\text{CH}_2\cdot$	+4.4
9	$\text{RCH}_2\text{CH}_2\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{RCH}=\text{CH}_2 + \text{CH}_3\text{CH}_2\cdot$	+0.4
10	$\text{R}\cdot + \text{R}\cdot \rightarrow \text{RH} + \text{RCH}=\text{CH}_2$	-51
11	$\text{R}\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{RH} + \text{CH}_2=\text{CH}\cdot$	+13

depolymerization developed by Tobolsky and others,²⁸ one should not find it difficult to accept the idea of depolymerization reactions being primarily responsible for the generation of more than one molecule per free radical at polymerization temperatures in the range of 200–300°C.

Free radicals can presumably be destroyed either by a combination reaction (EQUATION 7, TABLE 11), or by a disproportionation reaction (EQUATION 10, TABLE 12). Bevington²⁹ has made a study of the differences between the heat contents, entropies, and free energies of the products resulting from termination by combination, on the one hand, and termination by disproportionation, on the other. The products of several pairs of hydrocarbon free radicals were studied. Bevington's results indicate that, at the ethylene polymerization temperatures and pressures commonly employed, termination by combination is thermodynamically favored over termination by disproportionation. Largely for this reason, termination by combination is proposed as the principal termination step.

EQUATIONS 8 and 9 involve chain transfer to the monomer. The room temperature free energy change is not favorable. Since the entropy change is small, ΔF° is not much more favorable at polymerization temperature. It is doubtful that these reactions occur to a significant extent during ethylene polymerization.

As the free energy change is so unfavorable for reaction 11 and as the entropy change is very small, it is also unlikely that this reaction occurs frequently.

References

1. FAWCETT, E. W., R. O. GIBSON, M. W. PERRIN, J. G. PATON, & E. G. WILLIAMS. B.P. 471,590; U.S.P. 2,153,553.
2. STROTHER, C. O., B.P. 588,143.
3. FOX, J. J. & A. E. MARTIN. 1940. Proc. Roy. Soc. (A) **175**: 208.
4. THOMPSON, H. W. & P. TORKINGTON. 1945. Proc. Roy. Soc. (A) **184**: 3.
5. CROSS, L. H., R. B. RICHARDS, & H. A. WILLIS. 1950. Disc. Faraday Soc. **9**: 235.
6. BRYANT, W. M. D. 1947. J. Polymer Sci. **2**: 547.
7. RICHARDS, R. B. 1951. J. Appl. Chem. **1**: 370.
8. RAY, N. H. 1952. Trans. Farad. Soc. **48**: 809.
9. HARRIS, I. 1952. J. Polymer Sci. **8**: 353.
10. QUICK, Q. Carbide & Carbon Chemicals Co., So. Charleston, W. Va. Unpublished results.
11. HILL, F. N. & A. BROWN. 1950. Anal. Chem. **22**: 562.
12. MORAWETZ, H. J. 1951. J. Polymer Sci. **6**: 117.
13. RUGG, F. M., J. J. SMITH, & L. H. WARTMAN. 1953. J. Polymer Sci. **11**: 1.
14. BUNN, C. W. & T. C. ALCOCK. 1945. Trans. Faraday Soc. **41**: 317; BUNN, C. W. 1939. *Ibid.* **35**: 482.
15. HUNTER, E. & W. G. OAKES. 1945. Trans. Faraday Soc. **41**: 49.
16. RAINE, H. C., R. B. RICHARDS, & H. RYDER. 1945. Trans. Faraday Soc. **41**: 56.
17. PARKS, G. S. & J. R. MOSLEY. 1949. J. Chem. Phys. **17**: 691.
18. KRIMM, S. & A. V. TOBOLSKY. 1951. J. Polymer Sci. **7**: 57.
19. BUCKLEY, G. D., L. H. CROSS, & N. H. RAY. 1950. J. Chem. Soc.: 2714.
20. SUTHERLAND, G. B. B. M. & V. A. JONES. 1950. Disc. Faraday Soc. **9**: 281.
21. ELLIOT, A., E. J. AMBROSE, & R. B. TEMPLE. 1948. J. Chem. Phys. **16**: 877.
22. SMITH, D. C. 1948. Naval Research Lab. Report C-3274.
23. OAKES, W. G. & R. B. RICHARDS. 1949. J. Chem. Soc.: 2929.
24. WALL, J. 1948. J. Res. Nat. Bur. Stand. **41**: 315.
25. BROWN, A. & F. P. REDING. Carbide & Carbon Chemicals Co. So. Charleston. W. Va.
26. BRYANT, W. M. D. 1951. J. Polymer Sci. **6**: 359.
27. DAINTON, F. S. & K. J. IVIN. 1950. Trans. Faraday Soc. **46**: 331.
28. TOBOLSKY, A. V. 1944. J. Chem. Phys. **12**: 402; 1945. J. Phys. Coll. Chem. **47**: 77; 1945. J. Am. Chem. Soc. **67**: 785; 1946. J. Polymer Sci. **2**: 463.
29. BEVINGTON, J. C. 1952. Trans. Faraday Soc. **48**: 1045.
30. BUCKLEY, G. D. & N. H. RAY. 1952. J. Chem. Soc. : 3701.

STUDIES ON POLYVINYL CHLORIDE (II). BRANCHING*

By John D. Cotman, Jr.

Monsanto Chemical Company, Springfield, Mass.

Introduction

Elucidation of the ultimate detail of high polymer structure has for no single polymer been carried to completion. The examination of gross molecular properties by measurement of the viscosities, osmotic pressures and turbidities of dilute solutions of high polymers has resulted in characterization of many polymeric systems in terms of molecular weight and molecular weight distribution. The greatest extent of polymer characterization has been along these lines.

For any high polymer composed of a sequence of identical units, the possibility of several types of structural isomerism, at a single molecular weight, exists. The arrangement of identical units may differ in the order of bond formation between the basic building units of the monomer (head to head, head to tail, or random). The examination of a number of polymers¹ has revealed a marked preference for the orderly head to tail type of union. In systems with conjugated double bonds, the polymerization may lead to isomers corresponding to either 1,2 or 1,4 addition of monomer units, as well as cis-trans isomerism about the double bonds in the products of 1,4 addition of conjugated dienes. Polybutadiene fine structure² and the familiar structural isomerism distinguishing rubber and guttapercha exemplify these modes of isomerism.

The incorporation of bulky side groups in the monomer may limit free rotation about the polymer backbone and yield rotational isomers. The higher alkyl polyvinyl ethers have been convincingly demonstrated by Schildknecht *et al.*³ to polymerize to products of restricted internal chain rotation, highly ordered when prepared at low temperatures, and randomly oriented when polymerized at higher temperatures.

Finally, the build-up of three dimensional networks, by crosslinking and ramification from strictly linear chains to branched polymers, represents important structural variations.

Methods for the detection and measurement of extent of structural variation have been, in some instances, highly specific, *e.g.*, the determination of order of addition of monomer units in polyvinyl chloride by Marvel *et al.*^{1b} Most chemical studies on polymer structure are of necessity highly specific and limited. A variety of physical techniques of more general applicability can be utilized to indicate molecular isomerism of high polymers. Structural changes usually modify polymer dimensions and shape. Physical properties which are strongly dependent on molecular dimensions, *e.g.* intrinsic viscosities of polymers⁴ and the dissymmetry of light scattered from dilute polymer solutions,⁵ have been shown experimentally to deviate from established correlations with

* Considerable assistance in experimental procedures and instrumentation was given by G. C. Claver of the Monsanto Plastics Research Laboratory. Discussions with R. Buchdahl have been of invaluable assistance in the course of this research.

molecular weight when major changes in shape and polymer dimensions have been brought about by the introduction of unsaturation and/or branches. The development of quantitative correlations between the measured dimensional changes and the extent of branching has been accomplished in part.⁶

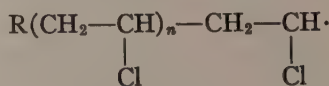
Lately, infrared spectroscopy has been used as an essentially analytical method of identification. The success of correlation of structural units with absorption bands is the limiting factor in its applicability.

The Branching of Polyvinyl Chloride

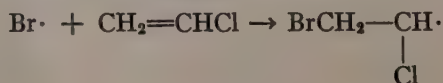
Staudinger and Schneiders⁷ ascribed the lower than theoretical chlorine content of several polyvinyl chloride fractions which they had prepared and the deviations of the measured values of intrinsic viscosity and molecular weight from a relationship $[\eta] = KM$ to chain branching. Fierz-David and Zollinger⁸ have since demonstrated that the low chlorine contents of polyvinyl chlorides are the result of thermal dehydrochlorination, not branching. Recent observations by Bengough and Norrish⁹ on the origin of the autocatalysis of vinyl chloride polymerization clearly indicate a chain transfer of growing polymer free radicals with previously formed polyvinyl chloride to yield a branched product. The data of Hayes¹⁰ confirm that polymer radicals from vinyl chloride are extremely reactive at this type of chain transfer and also that polyvinyl chloride is particularly susceptible to attack by free radicals. The material presented in this paper is a summary of attempts made at structural confirmation of branching already indicated in studies on polymerization kinetics and mechanisms.

The status of studies on solution properties of polyvinyl chloride is such that indications of branching from molecular dimensions are not readily accessible. Measurements of turbidity and osmotic pressure even in "good solvents" for this polymer are complicated by association of polymer molecules particularly for higher molecular weight fractions. Apparent molecular weights and dissymmetry measurements determined by turbidity studies¹¹ in cyclohexanone as well as butanone and dioxane suggest polymer association, thus limiting the determination of properties of individual molecules.

Examination of the chemistry of polyvinyl chloride polymerization leads to certain conclusions about the structure of the polymer. The active free radical in polymerization is, after addition of $n + 1$ monomer molecules,



where R is an initiator fragment. Directions of ionic and free radical addition of hydrogen bromide to vinyl chloride¹² indicate that electrophilic reactants add at the position of highest electron density¹³ to form unsaturated intermediates. For free radical addition of bromine:

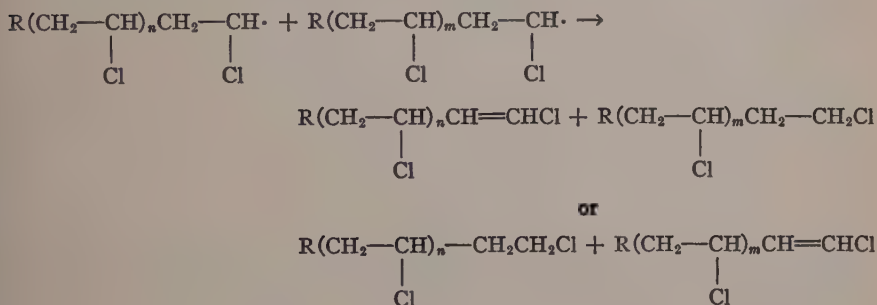


Chain carriers in the polymerization may react by alternative routes:

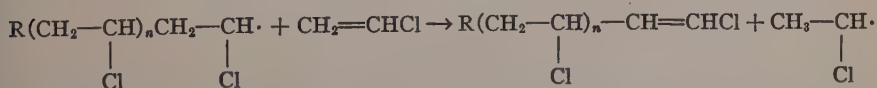
- Addition of monomer.
- Mutual termination by disproportionation or combination.
- Chain transfer with the monomer.^{14, 9}
- Chain transfer with polymer.⁹

These diverse reaction routes introduce several aspects of structural isomerism in polyvinyl chloride.

b. Termination by disproportionation most probably involves hydrogen abstraction from carbon adjacent to the reactive chloromethylene radical end:

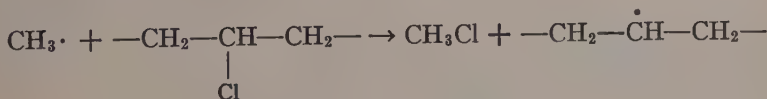


c. The chemical process involved in chain transfer with vinyl chloride monomer is somewhat more difficult to represent. Atom abstraction from the monomer, to yield $\cdot\text{CH}=\text{CHCl}$, $\text{CH}_2=\text{C}\cdot\text{Cl}$ or $\text{CH}_2=\text{CH}\cdot$, or hydrogen atom donation by the free radical to the monomer:

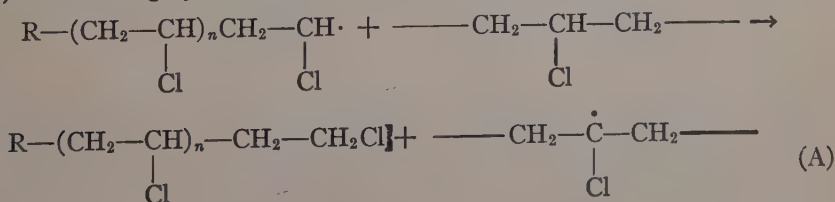


are possibilities. Intuitively, the latter mechanism is more acceptable.

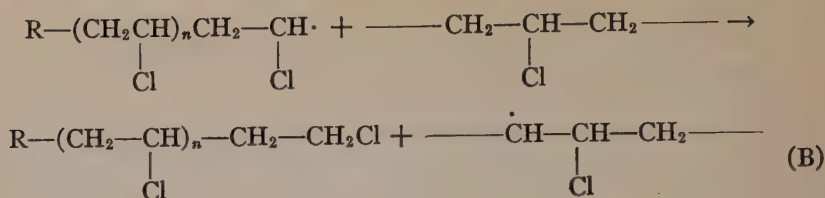
d. The work of Kenyon¹⁵ indicates the relative reactivities of the sites of previously formed polyvinyl chloride to free radical attack. The absence of methyl chloride among the products of methyl radical reaction with sec-butyl chloride demonstrates that the abstraction of chlorine atoms:



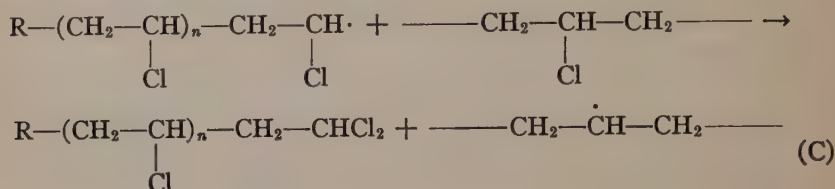
is a reaction of very low probability (as compared to removal of tertiary hydrogen). Reasoning by analogy, reactions such as:



and

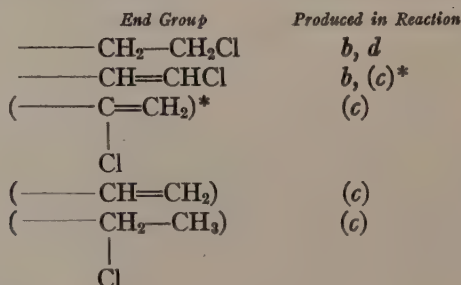


should predominate over the process:

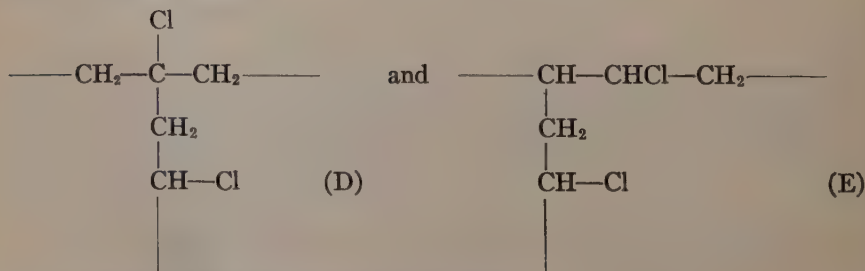


Kenyon has not interpreted his results as evidence for free radicals of the type (B) as well as (A). The ready free radical initiated dehydrochlorination of polyvinyl chloride, to yield runs of conjugated double bonds, is more easily rationalized in terms of radical (B) than (A). The similarity of structure (A) to the chain carrier for polymer growth suggests that the transfer process to produce (A) should be thermoneutral if not slightly exothermic.

As structural consequences of the termination and transfer reactions *b-d* we should find the end groups:



and the internal units:



* Products and reactions in brackets are less certain than the others.

Identification of the end group $\text{---CH}_2\text{---CH}_2\text{---Cl}$ and measurement of its concentration afford a method of indication of branches in polyvinyl chloride. This end group is produced by termination through disproportionation (Reaction *b*), and also by chain transfer to polymer (Reaction *d*). Termination of growing chains by disproportionation, combination of free radicals or transfer to monomer result, at most, in one $\text{---CH}_2\text{CH}_2\text{Cl}$ end group for every two polymer molecules. The $\text{---CH}_2\text{CH}_2\text{Cl}$ /molecule maximum of 0.5 corresponds to exclusive termination by disproportionation. Values of $\text{---CH}_2\text{CH}_2\text{Cl}$ /molecule in excess of 0.5, would clearly indicate branches in polyvinyl chloride. Identification of the internal units (D) or (E) corresponding to branch junctions would also confirm branches in polyvinyl chloride.

Unfortunately, the infrared spectrum of polyvinyl chloride (see FIGURE 1) is of such complexity that correlation of absorption bands with chemical

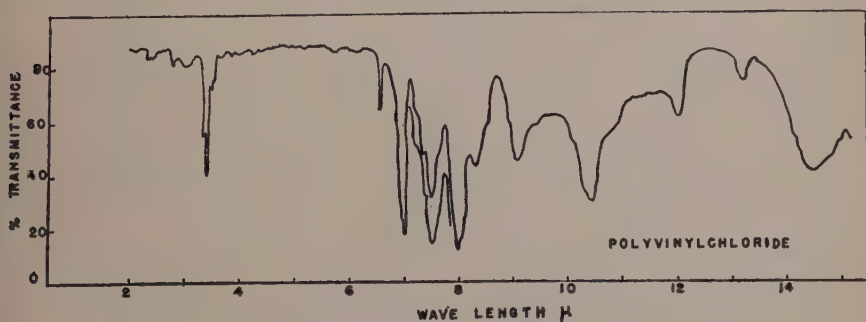
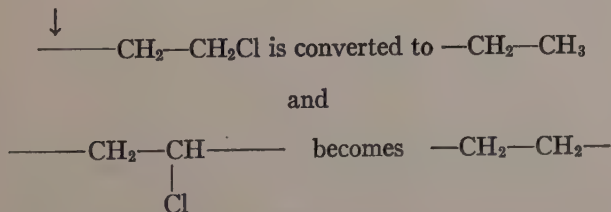


FIGURE 1. Infrared spectrum of polyvinyl chloride.

structure has not been particularly successful.¹⁶ On the other hand, reductive hydrogenation, with chlorine removal, yields a product (without appreciable chain degradation) which is identical in certain physical properties with polyethylene.¹⁷ The infrared spectrum of this product and of polyethylene are presented for comparison in FIGURE 2. It has been experimentally verified that primary chlorides are converted almost quantitatively to methyl groups and sec-chlorides to methylene units.

Thus:



As a consequence, identification of end groups corresponding to branch ends by infrared techniques applicable to hydrocarbons (*e.g.* polyethylene) presents a route to the estimation of extent of branching in polyvinyl chloride.

Procedure for the Estimation of Hydrocarbon Branching

Cross, Richards, and Willis¹⁸ observed changes in the 1378cm^{-1} methyl group absorption of polyethylenes on heating past the melting point. A doublet at 1350cm^{-1} and 1367cm^{-1} assigned to methylene groups increases in intensity as the crystallites are melted, attaining approximately constant intensity between $120\text{--}140^\circ\text{C}$., when the crystallites are completely melted. Measurements on octacosane have indicated the same behavior. Because of band overlap, the apparent intensity of the methyl group absorption reaches a constant value (at low CH_3/CH_2 ratios) only at temperatures above the melting point or in solution in suitable solvents, *e.g.* CCl_4 . The similarity of

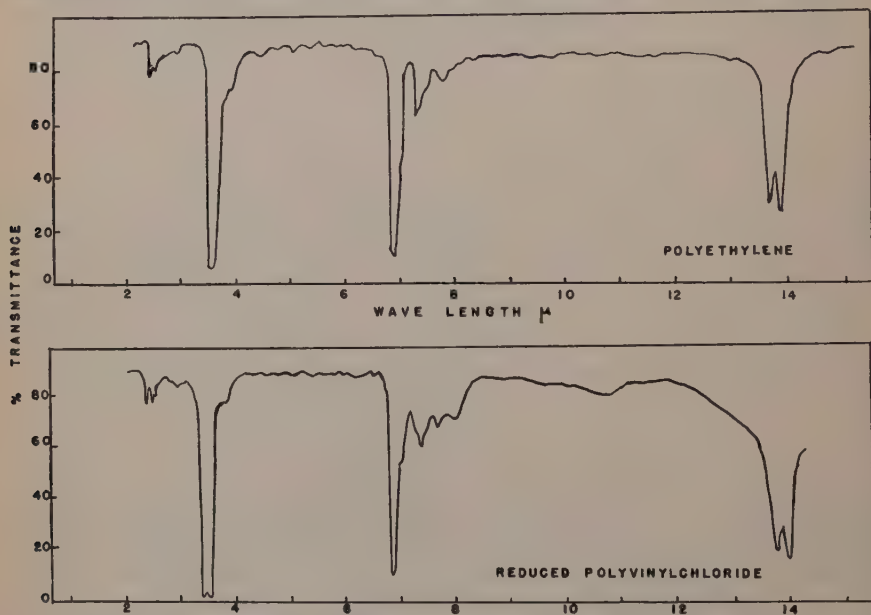


FIGURE 2. Infrared spectra of polyethylene(DYNH) and reduced polyvinylchloride.

absorption of molten octacosane and of a solution of this hydrocarbon in carbon tetrachloride (.364 M, 0.27 mm cell) is readily apparent from FIGURE 3.

The absorption of a number of low molecular weight hydrocarbons in the infrared between $1300\text{--}1500\text{ cm}^{-1}$ has been measured, both on the purified liquids, and on solutions in carbon tetrachloride at several concentrations. The cells employed were spaced with lead amalgam foil in fixed rigid mounts. Average cell thickness was determined from the spacing of interference fringes observed when the empty cells were placed in the specimen beam of a Perkin-Elmer, Model 21, double beam infrared spectrophotometer and run against air.¹⁹ The spectra of the hydrocarbons were measured either with the double beam spectrophotometer or point by point on a single beam Perkin-Elmer, Model 12B, spectrometer. In the determination of point by point absorption, the slits were set for 100 per cent scale readings against air, in the case of pure liquids, or against the cell filled with carbon tetrachloride for solutions. The

scattered radiation for a single rock salt cell element was found to be approximately constant at about 0.08 density units over the spectral interval scanned.

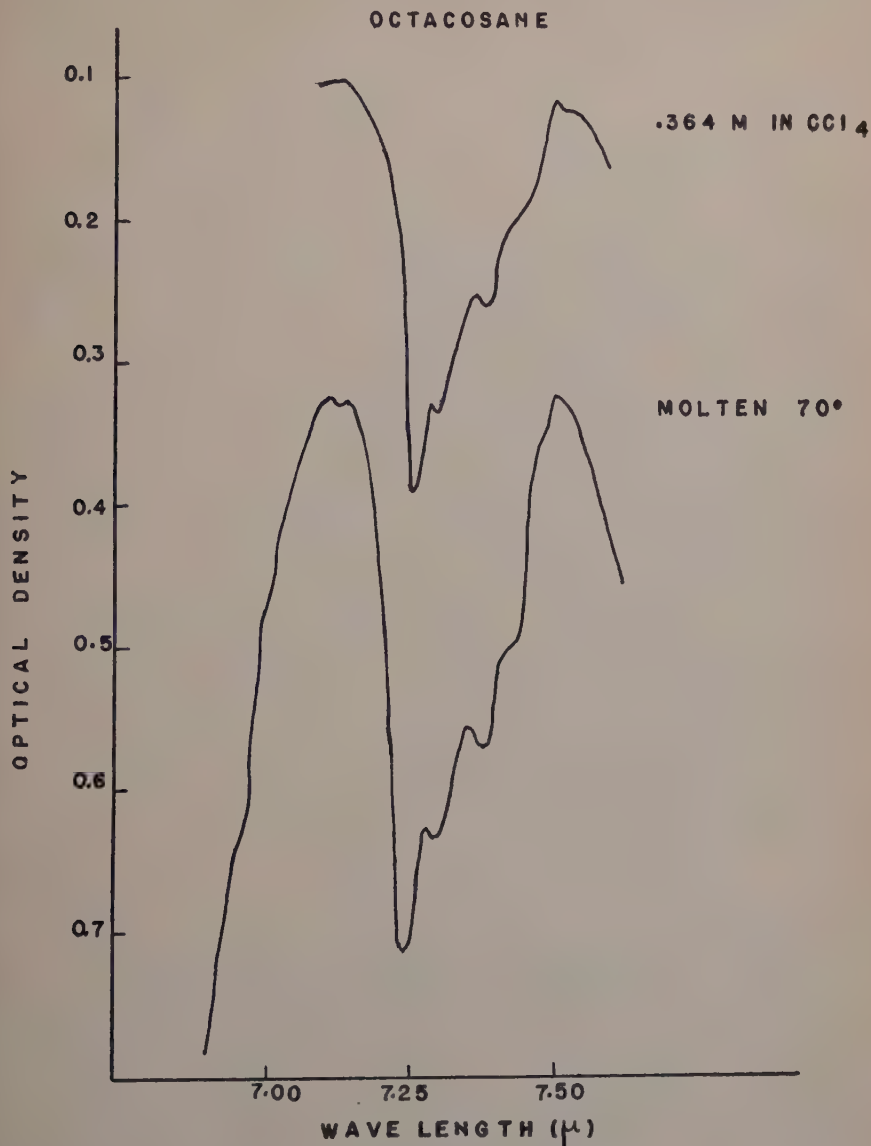


FIGURE 3. Methyl group absorption of molten octacosane and of octacosane in carbon tetrachloride solution.

Representative spectra for hexane, methyl cyclohexane and octacosane are presented in FIGURE 4.

Examination of the spectra, measured both for pure liquids and solutions in

carbon tetrachloride, revealed a constancy of the ratio of optical densities for maximum band absorption, for a particular hydrocarbon, at 1378 cm^{-1} and 1350 cm^{-1} , almost independent of the values of the individual band intensities.

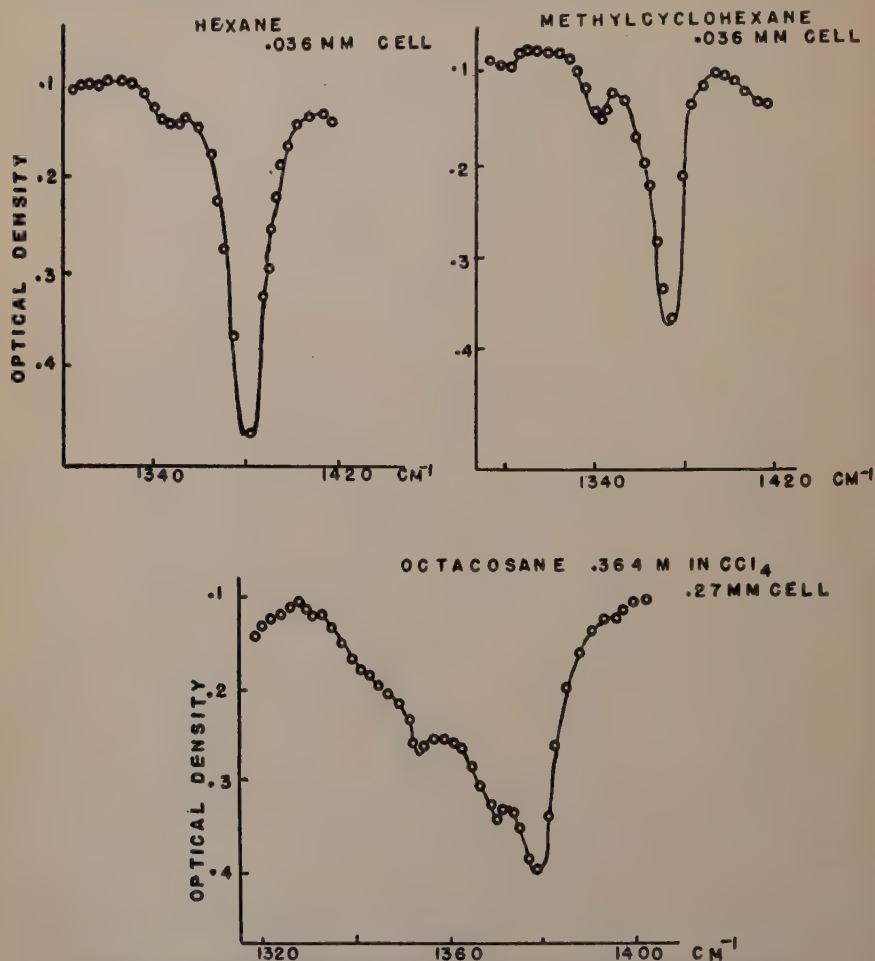


FIGURE 4. Methyl group absorptions of representative low molecular weight hydrocarbons.

Thus:

$$\frac{\log_{10} \left(\frac{T_0}{T} \right)_{1378}}{\log_{10} \left(\frac{T_0}{T} \right)_{1350}} = \frac{\epsilon_{1378} C_{\text{CH}_3}}{\epsilon_{1350} C_{\text{CH}_2}} = K \frac{C_{\text{CH}_3}}{C_{\text{CH}_2}}$$

where: T_0 , T are per cent transmittances in the absence and presence of absorbers respectively;

ϵ_{1378} and ϵ_{1350} are the absorption coefficients of the hydrocarbons at 1378 cm^{-1} and 1350 cm^{-1} ;

C_{CH_3} and C_{CH_2} are the concentrations, in moles/liter, of methyl groups and methylene groups.

$$K = \epsilon_{1378}/\epsilon_{1350}$$

$\log_{10} \frac{(T_0)}{(T)}$ 1378 and $\log_{10} \frac{(T_0)}{(T)}$ 1350 are optical densities at 1378 cm^{-1} and 1350 cm^{-1} respectively.

In the measurement of absorption, T_0 values were obtained by drawing a straight line between the wings of the band group at approximately 1300 cm^{-1} and 1400 cm^{-1} . Use of the ratio of densities eliminated the necessity of sample thickness measurement which is extremely difficult for melts of viscous polymers. It also yielded a direct value of the ratio $C_{\text{CH}_3}/C_{\text{CH}_2}$ which is referred to as the branching index of the hydrocarbon. An additional advantage of this method of measurement is that the ratio values were the same for samples measured on Model 21 and Model 12B instruments for which, at the gain levels employed, the spectral slit widths differed by a factor of approximately two.

A plot of the observed optical density ratios *versus* branching indices, for hydrocarbons with CH_3/CH_2 ratios varying from 0 to 0.5, is given in FIGURE 5, curve 1. The small reading of 0.48 for cyclohexane with $\text{CH}_3/\text{CH}_2 = 0$ is due to the fact that the short wavelength wing of the methylene doublet does not have zero intensity at 1378 cm^{-1} . The curvature of the plot indicates that the extinction coefficients of group absorptions for hydrocarbons are not constant. This aspect of intensity measurements has been discussed by Ramsey.²⁰ The absolute integrated intensities of methyl group absorption were, for low molecular weight hydrocarbons, constant and in good agreement with the values reported by Francis.²¹ To estimate the branching indices, CH_3/CH_2 values corresponding to the ratios of optical densities measured were read off of one of the curves of FIGURE 5. A plot of $\frac{A}{B}$ vs. $\frac{\text{CH}_3}{\text{Total Carbon}}$ is included as curve 2 of FIGURE 5.

Estimation of Branching Indices of High Molecular Weight Hydrocarbons²²

Films of polyethylene, or the polyhydrocarbon from polyvinyl chloride, were prepared by molding, solvent casting at 80° , followed by leaching, or by melting the polymer on the face of a rock salt plate. The specimen was mounted between rock salts in a cell of unique design²² which permitted the determination of infrared absorption at temperatures from well below 0° to approximately 200° in any desired atmosphere. For measurements on polyethylenes the surrounding gas was purified nitrogen. The spectrum was measured at room temperature and at a series of elevated temperatures. At temperatures above the melting range, the ratio of optical densities used for analysis was observed to attain a constant value. At lower temperatures, the intensities of the methylene doublet at 1350 cm^{-1} and 1367 cm^{-1} relative to the methyl group intensity at 1378 cm^{-1} increased with increasing temperature. The

branching indices for a number of polyethylenes were 20-40 as has been reported.¹⁸

A commercial polyvinyl chloride of D.P. = 1423 (D.P. = degree of polymerization) was separated by extraction into three fractions: Fraction I, soluble in benzene; Fraction II, soluble in a solvent mixture, benzene: butanone = 10:1; and Fraction III the residue after extraction of Fraction II. The D.P. values of these fractions were: Fraction I, D.P. = 426; Fraction II, D.P. = 681; Fraction III D.P. = 1830.

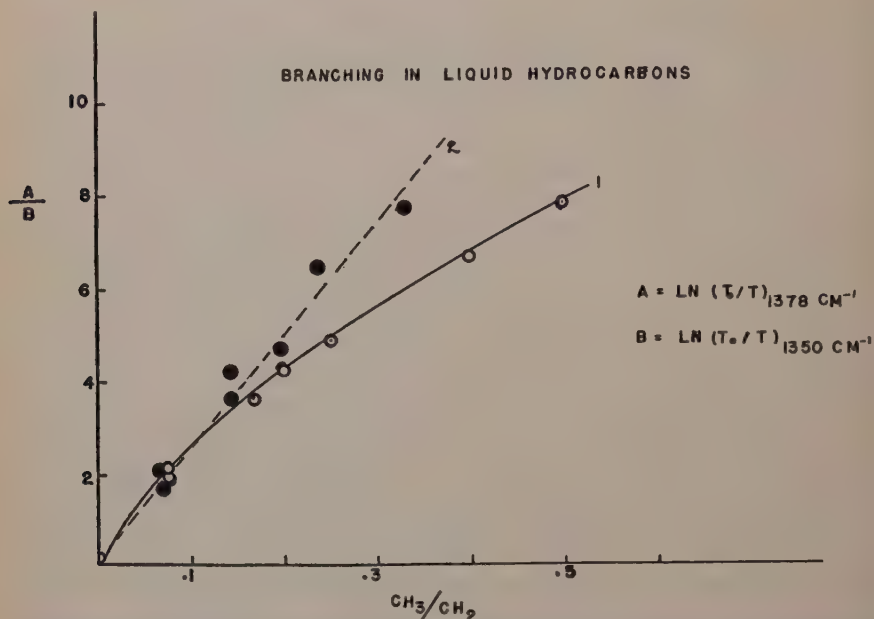


FIGURE 5. Calibration curves for the estimation of CH_3/CH_2 ratios (curve 1) and $\text{CH}_3/\text{total carbon}$ (curve 2) for hydrocarbons.

Hydrogenation of the unfractionated polyvinyl chloride yielded a polyhydrocarbon A. Reduction of Fractions I, II and III resulted in polyhydrocarbons AI, AII, and AIII respectively. In each instance, the extent of hydrogenation was from 96-99 per cent. Chlorine contents of the polyhydrocarbons as well as chloride ion liberated by reduction were measured to establish the extents of conversion.

The infrared spectra of the polyhydrocarbons were all similar to that of A which has been reproduced in FIGURE 2. Infrared absorption spectra between $1320\text{--}1400 \text{ cm}^{-1}$ are presented in FIGURE 6 along with the absorption curve of cyclohexane. Comparison of the band contours for those several hydrocarbons reveals that, in general band shape, the spectra of the polyhydrocarbons are more like polyethylene and the low molecular weight hydrocarbons containing methyl groups than that of the methyl free cyclohexane. The single absorption maximum of cyclohexane at 1350 cm^{-1} appears as a doublet at 1350

cm^{-1} and 1367 cm^{-1} in all of the methyl containing hydrocarbons. The polyhydrocarbon specimens do not have completely resolved maxima at 1378 cm^{-1} and 1367 cm^{-1} as do octacosane and polyethylene. The 1367 cm^{-1} branch of

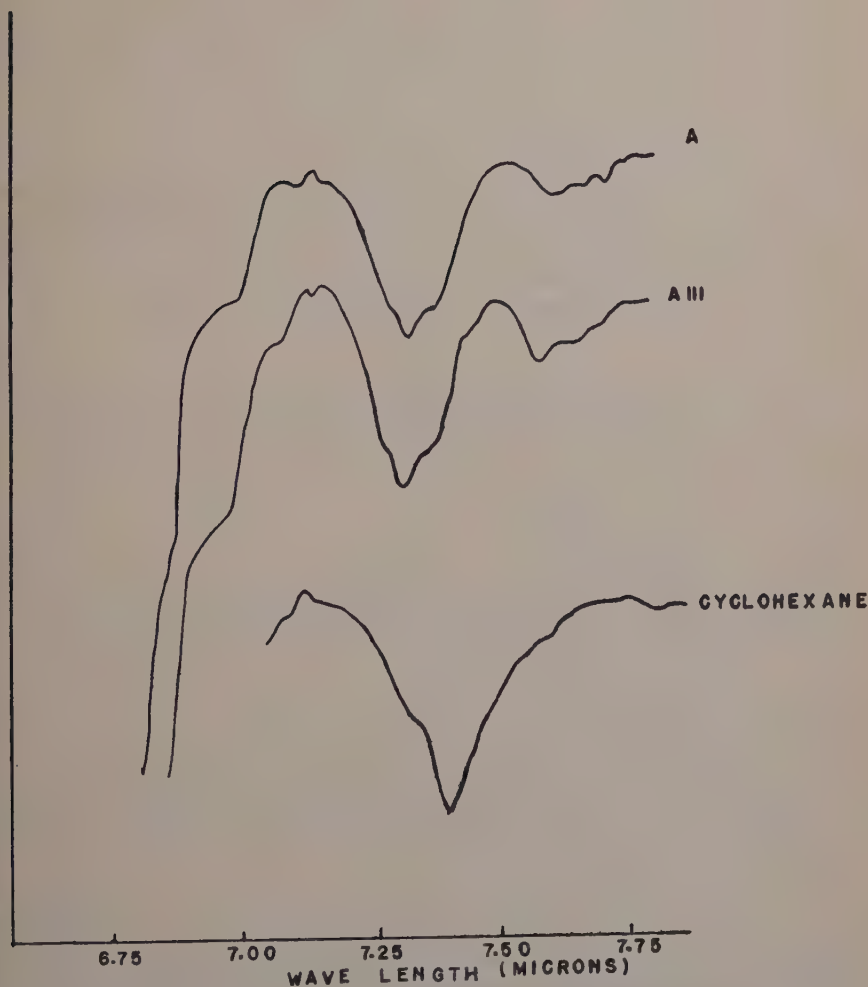


FIGURE 6. Absorption spectra for reduced polyvinylchlorides and for cyclohexane in the 7.00-7.50 micron region.

the doublet has, however, for these polymers, a shoulder at about the frequency corresponding to methyl absorption. Moreover, for the molten specimens, the 1367 cm^{-1} portion of the doublet is more intense than the 1350 cm^{-1} band, a characteristic of polyethylene. In the absence of other interfering absorption, such spectra indicate the presence of methyl groups at a much lower concentration than is found in most polyethylenes.

Before it could be concluded that methyl groups were present in the polyhydrocarbon, the absence of interfering absorption by other structural units had to be established. The presence of a very low concentration of double bonds in the polyhydrocarbon, probably the result of thermal dehydrochlorination of polyvinyl chloride,⁸ has been established from infrared spectra of very thick samples. Double bonds have not been observed²³ to result in absorption at 1378 cm^{-1} . Similarly, residual chlorine should not result in substantial absorption at the wave lengths under consideration; for, even for polyvinyl chloride, the spectral interval $1375\text{--}1385\text{ cm}^{-1}$ is relatively transparent. In addition, absorption characteristic of polyvinyl chloride of greater relative intensity is of very low intensity in the polyhydrocarbon. From the relative optical densities of the intense band at 1250 cm^{-1} and the optical density at 1378 cm^{-1} for polyvinyl chloride, as well as the relative intensities of the 1250 cm^{-1} absorptions in polyvinyl chloride and a product hydrogenated to 95 per cent, it has been possible to estimate that the optical density at 1378 cm^{-1} corre-

TABLE 1
BRANCHING IN POLYVINYL CHLORIDE

Sample	Wt % of A	D.P.	$\frac{(\text{Optical density})^\dagger 1378\text{ cm}^{-1}}{(\text{Optical density}) 1350\text{ cm}^{-1}}$	$\frac{\text{CH}_3}{\text{CH}_2} \times 10^3$	Branches/ molecule
A	—	1423	0.67	7	20
AI	11	426	0.72	11	9
AII	22	681	0.68	8	11
AIII	67	1830*	0.55	4	15

* D.P. calculated from rel. wts. of fractions and D.P. values of A, AI and AII.

† These are the average optical density ratios for measurements on several samples of each polyhydrocarbon. The actual optical densities at the individual wave lengths were approximately 0.07–0.19 for 1378 cm^{-1} and 0.1–0.26 for 1350 cm^{-1} . The average scatter of individual values about the mean optical density ratios was approximately 10 per cent with the worst scatter about 20 per cent.

sponding to residual polyvinyl chloride structure should be no more than 0.01–0.02. Other structural differences from polyethylene are substantially absent. For these reasons it was concluded that there are methyl groups in the polyhydrocarbon obtained from polyvinyl chloride. These groups are present at much lower concentrations than usually encountered in polyethylenes.

Results and Discussion

The data leading to estimates of branching indices for the several polyvinyl chloride specimens and the relative numbers of branches/average molecule are listed in TABLE 1.

A second indication of the presence of branches in polyvinyl chloride was observed in the spectra of relatively thick 0.25 mm films of the polyhydrocarbons measured at room temperature. In the measurement of branching indices, thinner specimens, 0.025–0.075 mm, were studied. At these thicknesses, bands which could be associated with double bands were very weak. For 0.25 mm films, however, several distinct bands of medium intensity in the spectral range $700\text{--}1000\text{ cm}^{-1}$ which could be correlated with double bands

were observed. Of particular interest was absorption in the range 800–900 cm^{-1} . Cross *et al.*,¹⁸ and McMurry and Thornton²⁴ have correlated absorption of low intensity at 844–890 cm^{-1} with methyl groups in long chain hydrocarbons. In addition, an angular out-of-plane CH—deformation for trisubstituted double bonds²³ has been correlated with absorption in the spectral interval 801–883 cm^{-1} . The 801–833 cm^{-1} band is definitely present in the spectra of 0.25 mm

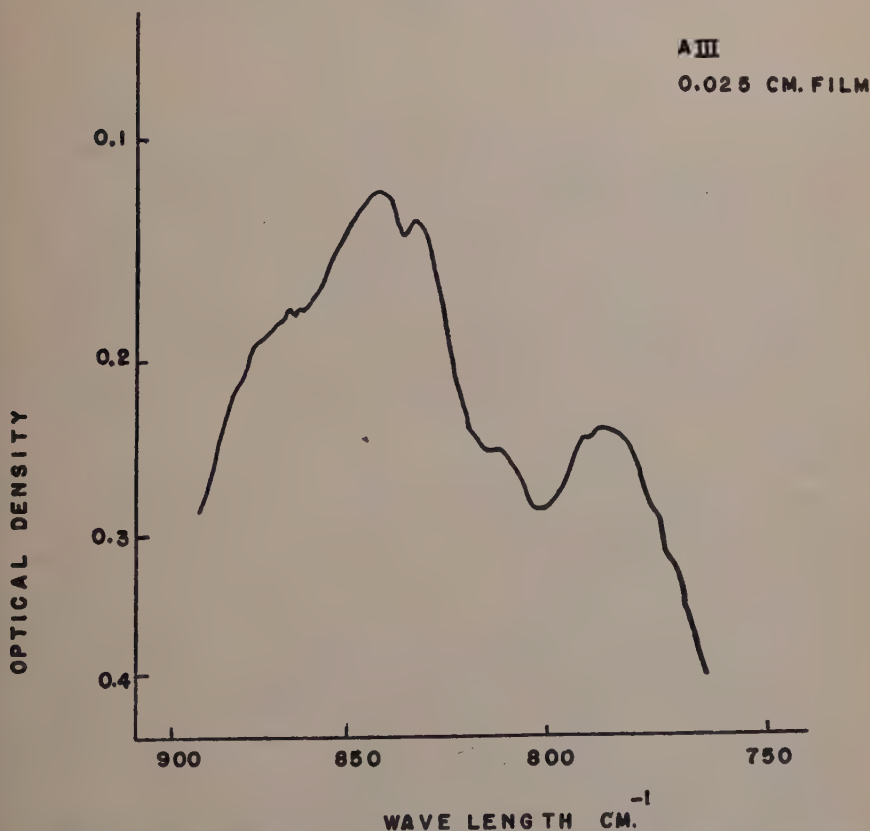
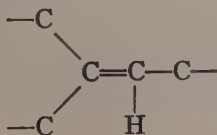


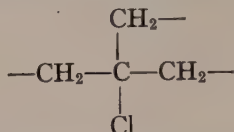
FIGURE 7. Infrared evidence for the presence of trisubstituted double bonds in fraction AIII reduced polyvinylchloride.

samples of the polyhydrocarbons (see FIGURE 7). In the absence of precise calibration data, the estimation of



concentrations was not tabulated for the specimens of TABLE 1. An estimate

of the $\frac{\text{tertiary (C=C)}}{\text{CH}_2}$ ratio of AIII, using the extinction coefficient of McMurry and Thornton²⁴ for 810 cm^{-1} absorption, yields a value 2×10^{-3} . Although the CH_3/CH_2 index has been already estimated as 4×10^{-3} , the lower result from double band concentration is not inconsistent. The tertiary structure:



is more sterically hindered toward replacement of chlorine by hydrogen than primary or secondary structures. A competing reaction, occasional loss of hydrogen chloride by thermal dehydrochlorination, could easily be far from complete, converting only a fraction of the branch junctions into tertiary double bonds.

The presence of CH_3 groups cannot be unequivocally established from absorption between 844–895 cm^{-1} . There is definite absorption in this wavelength region. The proximity of a more intense unsaturation band (relative values of intensities given by McMurry and Thornton²⁴ are 120/1 with the unsaturation absorption more intense) obscures the very weak methyl group absorption.

From these observations on the infrared spectrum of the polyhydrocarbons derived from polyvinyl chloride, it can safely be concluded that structural evidence confirms the kinetic observations. The numerical values of branching indices point to rather extensive branch formation. The values for extent of branching are subject to large errors because the analytical procedure has been extended into a concentration range where precision and accuracy are very limited. The primary weaknesses of the measurement of CH_3/CH_2 ratios stem from the relatively weak methyl group absorption, and the uncertainties of extrapolation. The two spectral indications of branching give estimates of the number of branches which differ by a factor of two. The estimate based on tri-substituted double bonds could be too low.

The values of branches per molecule correspond roughly to molecular weights of 3000–7600 per branch unit. Such values for polymer molecules with molecular weights between 26,500 to 115,000 suggest, as do the results of Bengough and Norrish,⁹ that an appreciable portion of chain propagation occurs on the relatively immobile free radicals emanating from the previously formed polymer. The structural observations thus complement the kinetic results and point to a significantly branched polymer. There is a stoichiometric inconsistency in the average number of branches/molecule for the unfractionated polymer and the weighted values for the fractions. Loss of the very low molecular weight portion of the polymer during fractionation and errors of analysis could cause such disagreement.

References

- 1a. STAUDINGER, H. & A. STEINHOFFER. 1935. *Ann.* **517**: 35.
- 1b. MARVEL, C. S., J. H. SAMPLE & M. ROY. 1939. *J. Am. Chem. Soc.* **61**: 3241.

- 1c. STAUDINGER, H. & W. FEISST. 1930. *Helv. Chim. Acta.* **13**: 832.
- 1d. MARVEL, C. S. & C. E. DENOON. 1938. *J. Am. Chem. Soc.* **60**: 1045.
- 1e. MARVEL, C. S. & C. L. LEVESQUE. 1938. *J. Am. Chem. Soc.* **60**: 280; 1939. *Ibid.* **61**: 3234.
2. MEYER, A. 1949. *Ind. Eng. Chem.* **41**: 1570.
3. SCHILDKNECHT, C. E., *et al.* 1948. *Ind. Eng. Chem.* **40**: 2104.
4. YOUNGSON, G. & H. W. MELVILLE. 1950. *J. Chem. Soc.*: 1613.
5. THURMOND, B. D. & B. H. ZIMM. 1952. *J. Polymer Sci.* **8**: 477; BIER. 1949. *Die Makromolecular Chemie.* **4**: 41.
6. ZIMM, B. H. & W. H. STOCKMAYER. 1949. *J. Chem. Phys.* **17**: 1301.
7. STAUDINGER, H. & J. SCHNEIDERS. 1939. *Ann.* **541**: 151.
8. FIERZ-DAVID, H. & H. ZOLLINGER. 1945. *Helv. Chim. Acta.* **28**: 463.
9. BENGOUGH, W. & R. NORRISH. 1949. *Nature.* **163**: 325; 1950. *Proc. Roy. Soc. (A)* **200**: 301.
10. HAYES, R. 1952. Abstracts ACS Meeting.
11. Unpublished observations. Monsanto Chemical Company; DOTY, P., R. H. WAGNER, & S. SINGER. 1947. *J. Phys. & Colloid Chem.* **51**: 32.
12. KHARASCH, M. S. & C. HANNUM. 1934. *J. Am. Chem. Soc.* **56**: 1782.
13. WHELAND, G. W. *The Theory of Resonance.* : 130. Wiley. New York.
14. NOZAKI, K. 1947. *Disc. Faraday Soc.* **2**: 337.
15. KENYON, A. 1952. *J. Am. Chem. Soc.* **74**: 3372.
16. THOMPSON, H. W. & P. TORKINGTON. 1945. *Proc. Roy. Soc. (A)* **184**: 21.
17. COTMAN, J. D., JR. Unpublished observations.
18. CROSS, L. H., R. B. RICHARDS, & H. A. WILLIS. 1950. *Disc. Faraday Soc.* **9**: 235.
19. SMITH, D. C. & E. MILLER. 1944. *J. Opt. Soc. Am.* **34**: 130.
20. RAMSEY, D. 1952. *J. Am. Chem. Soc.* **74**: 72.
21. FRANCIS, S. 1950. *J. Chem. Phys.* **18**: 861.
22. CLAVER, G. Unpublished observations.
23. SHEPPARD, N. & D. SIMPSON. 1952. *Quarterly Reviews.* **6**: 1.
24. MCMURRY, H. & V. THORNTON. 1952. *Anal. Chem.* **24**: 318.

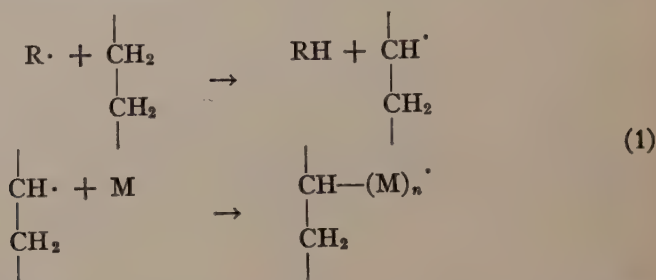
BRANCHING IN DIENES*

By Maurice Morton

University of Akron, Ohio

Introduction

Considerable interest has been shown recently in the possibilities of interaction between free radicals and polymer chains during the course of a polymerization reaction. In the case of vinyl polymerizations, where the monomer possesses only one double bond, such a reaction is generally considered to lead to chain transfer from radical to polymer, resulting in the growth of a branch on the original polymer chain. For a hydrocarbon polymer this branching reaction may be visualized as follows:

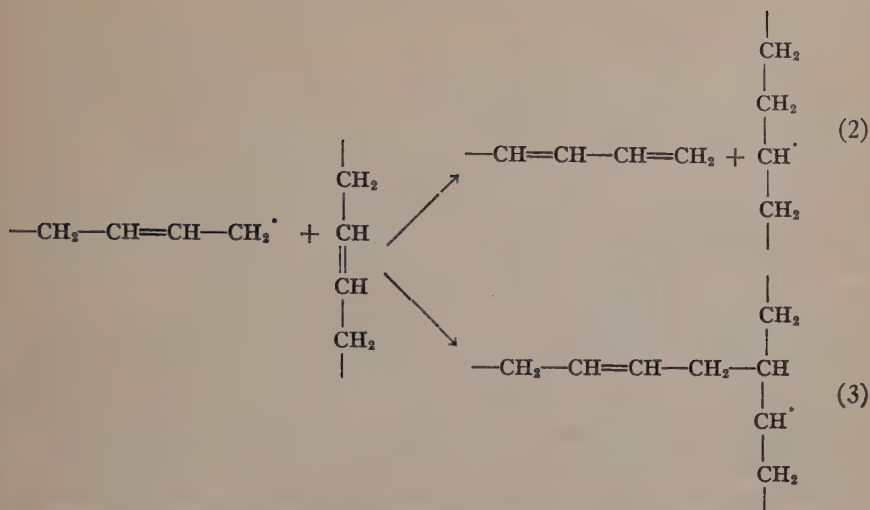


where R' represents a free radical and M refers to a monomer molecule. The presence of branches on this type of polymer chain has been quite well established.

In the case of polydienes, the situation is considerably more complex because of the presence of residual double bonds in the polymer chain. Thus, in addition to the branching reaction shown above, there is also the possibility of branched structures arising from an interaction between a free radical and a polymer double bond. This can be exemplified by the possible reactions (2 and 3) for polybutadiene (see page 433).

It can be seen that reaction (2) is simply another type of transfer reaction leading to the formation of a branched polymer chain. Reaction (3), however, is not a transfer reaction, but involves the *addition* of a growing chain to an already-formed polymer chain. Flory¹ has termed this reaction "crosslinking" and has pointed out that it is this type of reaction which can lead to the rapid formation of large networks characterized by insolubilization of the polymer. Reactions (1) and (2), although leading to a distortion of the molecular weight distribution, cannot, by themselves, lead to the formation of large networks of the gel type. It might be added that reactions (2) and (3) are oversimplifications since they show only the 1,4 structure of the polymer chain, whereas

* Experimental data contained in this paper were obtained in investigations carried out under the sponsorship of the Office of Synthetic Rubber, Reconstruction Finance Corporation, in connection with the U. S. Government Synthetic Rubber Program.



actually similar reactions can occur with a 1,2 structure, and this fact must be taken into consideration.

It becomes apparent, therefore, that a measurement of the extent of reactions (1) and (2) presents considerable difficulty since it involves a knowledge of the extent of branching in the polymer chain. Reaction (3), however, leads to a relatively easily measured parameter *i.e.* the gel point.

Crosslinking and Network Formation in Dienes

In discussing the crosslinking reaction of type (3) above, Flory¹ has suggested a simple kinetic treatment involving the relative reactivity of polymer *versus* monomer double bonds with the growing free radical. This leads to the following rate expression:

$$\frac{dv}{d\alpha} = \frac{2K\alpha}{(1 - \alpha)} \quad (4)$$

where v = proportion of crosslinked units (expressed as moles of crosslinked units per mole of initial monomer.)

α = fractional extent of conversion of monomer to polymer

$K = k_3/k_2$

k_2 = velocity constant for normal chain propagation

k_3 = velocity constant for crosslinking.

Hence, it is apparent that the degree of crosslinking of polymer chains is a function of the extent of polymerization. Furthermore, from statistical considerations,² it can be predicted that the first appearance of an insoluble network occurs when there is one crosslinked unit per primary chain molecule,* on a weight-average basis. This should make it possible, by appropriate measure-

* The term "primary molecule" is used to designate the original polymer chain before any crosslinking reactions occur. The above statistical treatment is valid only for a random distribution of crosslinked units,¹ but is applicable up to 60 to 70 per cent conversion.

ments of the conversion at which gel makes its appearance, to calculate K , the relative rate of the crosslinking reaction. It should be stated, at this point, that K is a measure of the reactivity of both types of double bond present in a polydiene *i.e.* internal (1,4) and external (vinyl). Since, however, it has been definitely established³ that, in free radical polymerization, the ratio of these two bonds is largely independent of temperature or extent of conversion, the value of K can be taken as representing their combined reactivity.

Hence, for a quantitative determination of the relative crosslinking rate it is necessary to establish with reasonable accuracy the following two parameters:

- (a) The extent of conversion at which the first "infinite network," or gel, appears;
- (b) The molecular weight (weight-average) of the primary chains at the gel-point.

It should be stressed that, for the required calculation of the crosslinking rate, an actual measurement of the weight-average molecular weight at incipient gelation would not be reliable, due to distortion of the molecular weight distribution by crosslinking of chains, or, possibly, by some branching reactions as well. The primary chain length must be deduced from the known kinetics of the system, without being obscured by further polymer-radical reactions.

The determination of the above parameters in ordinary homogeneous polymerization systems, either bulk or solution, presents considerable difficulty. In the first place, free radical catalyzed polymerization of butadiene or isoprene is extremely slow even in bulk systems. Furthermore, detailed knowledge of the kinetics is not available for purposes of calculating primary chain length, and exact determination of gel-points is difficult. The emulsion polymerization system, on the other hand, offers several advantages in this regard. It makes possible reasonably rapid rates of polymerization, and the mechanism and kinetics of this system have been the subject of intensive study during recent years. Furthermore, the practical use of certain aliphatic thiols for control of chain length by chain transfer makes it possible to control and determine quite accurately the gel-point in emulsion polymerization systems.

Crosslinking in Emulsion Polymerization

The mechanism of emulsion polymerization has been greatly elucidated in recent years, thanks largely to the work of Harkins and his collaborators.⁴ In the case of water-insoluble monomers, emulsion polymerization occurs in three well-defined stages. The first stage involves the initiation of polymer nuclei largely from monomer dissolved within soap micelles, and ceases at an early stage due to depletion of soap from the micelles by adsorption on the polymer-water interface. The second stage consists of growth of the polymer particles, which are kept in a swollen state by monomer diffusing from the free monomer phase. This continues until the free monomer phase disappears (about 50–60 per cent conversion for butadiene) and all the remaining monomer is inside the polymer particles. This last constitutes the third stage in emulsion polymerization.

According to this mechanism, it has been estimated⁴ that 99 per cent of the polymer is formed during growth of the polymer particles. Up to 50–60 per cent conversion this growth occurs in polymer particles in the presence of a free monomer phase. Thus, for any kinetic interpretation, it is necessary to know the monomer-polymer relationship within these particles. Recent work in this laboratory has shown that the diffusion rate of the monomer into the polymer particles is apparently rapid enough to maintain them in a saturated condition. The saturation equilibrium is apparently governed by a balance between the swelling force of the particles and the interfacial energy, and is not very sensitive to changes in the size of the particles during growth in any given system. It may be considered, therefore, that the monomer-polymer ratio in the particles remains practically constant as long as any free monomer phase is present. This accounts for the fact that the rate of polymerization is linear with time over a large portion of the reaction.

FIGURES 1 and 2 show typical rate curves obtained in the persulfate-catalyzed emulsion polymerization of butadiene and isoprene. It can be seen that the rate is zero-order at least up to 50–60 per cent conversion in accord with the proposed mechanism. All of these polymerizations were carried out in the presence of a suitable thiol, without which the persulfate does not initiate the polymerization of these dienes except at a very slow rate.

This condition of constant monomer concentration at the locus of polymerization requires a modification of the crosslinking rate equation to the following form:

$$\frac{dv}{d\alpha} = \frac{2K}{m}$$

where m = monomer-polymer ratio in the particles.
The integrated form then becomes

$$\rho = \frac{v}{\alpha} = \frac{2K}{m} \quad (5)$$

where ρ is, by definition, the proportion of crosslinked units in the polymer, chains.

Under such conditions, the frequency of crosslinks in the chain remains constant as long as the monomer-polymer ratio is maintained constant. Formation of an infinite network will then depend only on the magnitude of the primary chain length.

Primary Chain Length in Emulsion Polymerization

The use of certain aliphatic thiols as molecular weight regulators ("modifiers") has become a widespread practice. They have been found especially useful in suppressing gel formation in diene polymerization, presumably by preventing the chains from reaching sufficient length to lead to formation of infinite networks. It has been found^{5, 6} that the chain-transfer reaction between the growing chains and the thiol is by far the most predominant mechan-

ism of chain termination and that approximately one molecule of thiol is consumed for every chain. Hence, a kinetic study of the disappearance of the thiol enables a calculation of the primary chain length formed. Because of the zero-order rate of polymerization it can be expected that the rate of disappearance of the thiol should be first-order. This has been found to be the case for several thiols^{7, 8, 9} whose rate of disappearance can be expressed as follows:

$$-\frac{dR}{d\alpha} = rR \quad (6)$$

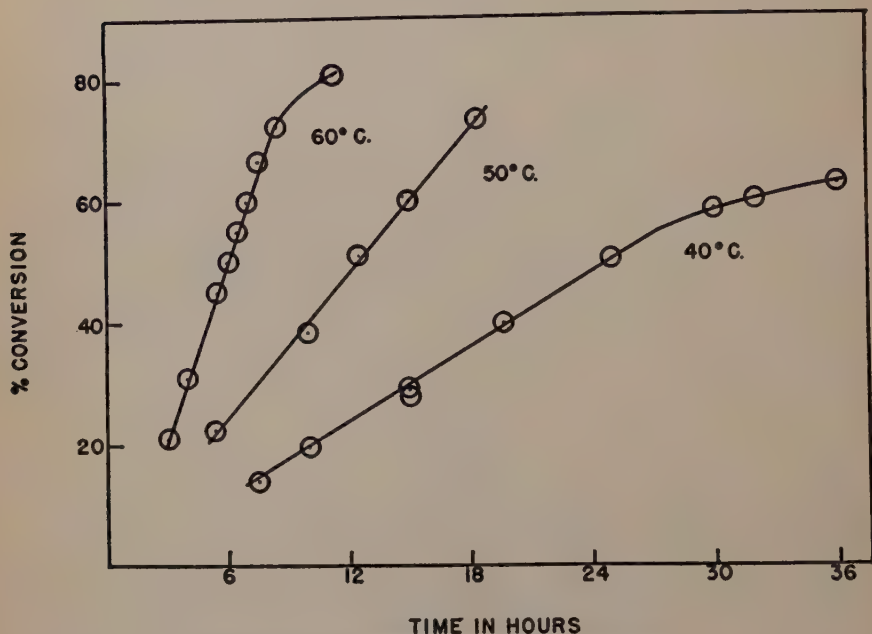


FIGURE 1. Rate of emulsion polymerization of butadiene.

where R = concentration of thiol, expressed as moles per mole of initial monomer

r = a constant (sometimes called "regulating index").

On the basis of such a mechanism, Bardwell and Winkler¹⁰ have recently applied a statistical treatment to obtain the molecular weight distribution. They derived the following expression for the weight-average degree of polymerization:

$$\bar{y}_w = \frac{2}{\alpha r R_0} (e^{r\alpha} - 1) \quad (7)$$

where \bar{y}_w = cumulative weight-average degree of polymerization at any given conversion (α)

R_0 = initial concentration of thiol, in the same units as R in EQUATION 6.

Thus, it becomes possible to calculate the primary chain length from known data on the rate of disappearance of the chain-transfer agent.

Some data on the behavior of a thiol in the persulfate-catalyzed emulsion polymerization of butadiene and isoprene are shown in FIGURES 3 and 4. The thiol used was a commercial material, Sulfole B-8, from the Phillips Petroleum Company. It consists of a mixture of isomeric tertiary mercaptans of the undecyl variety. From these first-order plots, which are valid up to about 50 per cent conversion, it is possible to calculate, in each case, the value of the weight-average primary chain length by means of EQUATION 7.

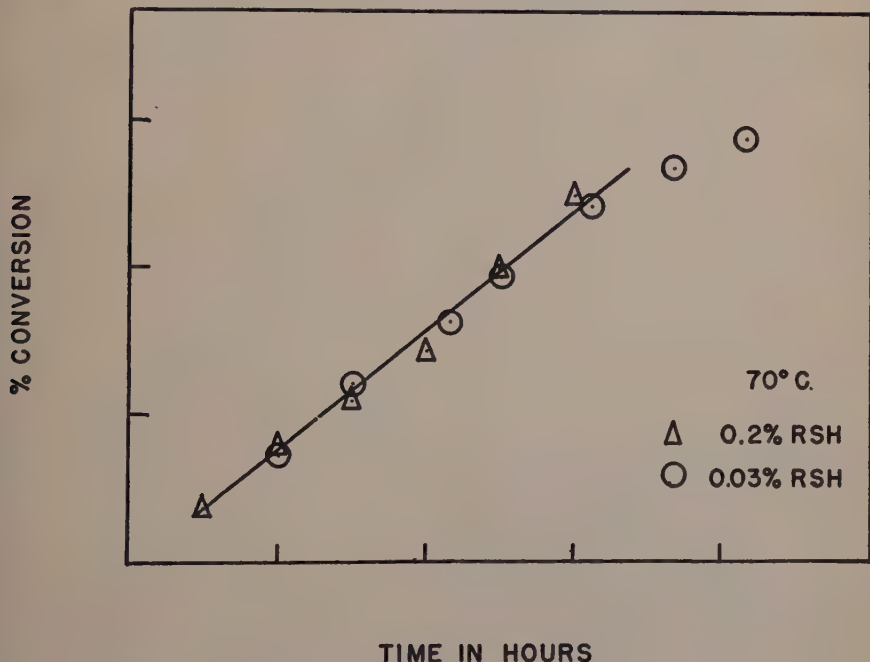


FIGURE 2. Rate of emulsion polymerization of isoprene.

Gel-points in Emulsion Polymerization

The last remaining parameter to be evaluated in this crosslinking rate study is the gel-point conversion. This, ordinarily, is quite difficult to determine accurately for several reasons. The high degree of unsaturation of polydienes renders them susceptible to oxidative crosslinking, hence networks may be formed during any precipitation or drying of the polymer. Furthermore, the gel which first appears in these polymers is, of course, very lightly crosslinked and hence quite easily ruptured mechanically, rendering observation difficult. Permitting the polymerization to continue toward higher degrees of crosslinking results in a "tighter" gel which is more easily handled and observed. It has been a popular practice in emulsion polymerization of dienes, to indicate the gel-point by a plot of the intrinsic viscosity of the polymer, in a suitable solvent,

against the conversion, after first carrying out a sol-gel separation. Since gelation involves the higher molecular weight species preferentially, the soluble portion shows a lower intrinsic viscosity, the maximum in the viscosity-conversion curve showing a lower intrinsic viscosity, the maximum in the viscosity-conversion curve corresponding to the gel-point. Here again, however, the sol-gel

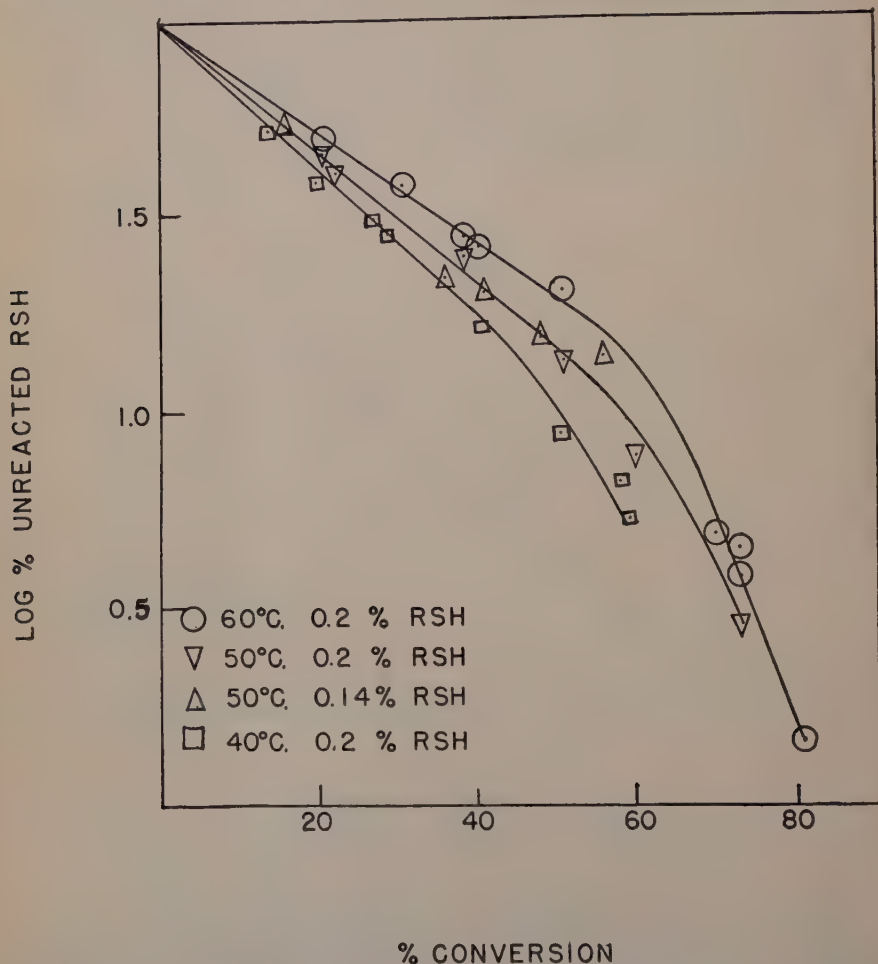


FIGURE 3. Rate of RSH disappearance in butadiene polymerization.

separation process is very difficult to carry out in the vicinity of the gel-point, so the exact location of the peak in the viscosity curve is problematical.

In emulsion systems, it is obvious that the size of an "infinite network" is limited by the size of the individual polymer particles. Hence, the gel here will be in the form of "microgel," as proposed by Baker.¹¹ Presumably, during coagulation and drying, this microgel is interlinked into "macrogel," *i.e.* an insoluble, visible gel structure. The extent, however, to which all the microgel

is coalesced into a single network is dependent upon the treatment it receives during coagulation and drying. It is obvious that a greater or lesser extent of the microgel may be redispersed in a solvent under the conditions of a sol-gel separation. For the purpose of accurately detecting the gel-point, it is probably best to avoid the complications involved in coagulation and drying of the polymer, and to use the "Vistex" technique of dispersing the latex directly into a compatible solvent (*e.g.* benzene-isopropanol). The modification of this method suggested by Henderson and Legge¹² is very useful for this purpose,

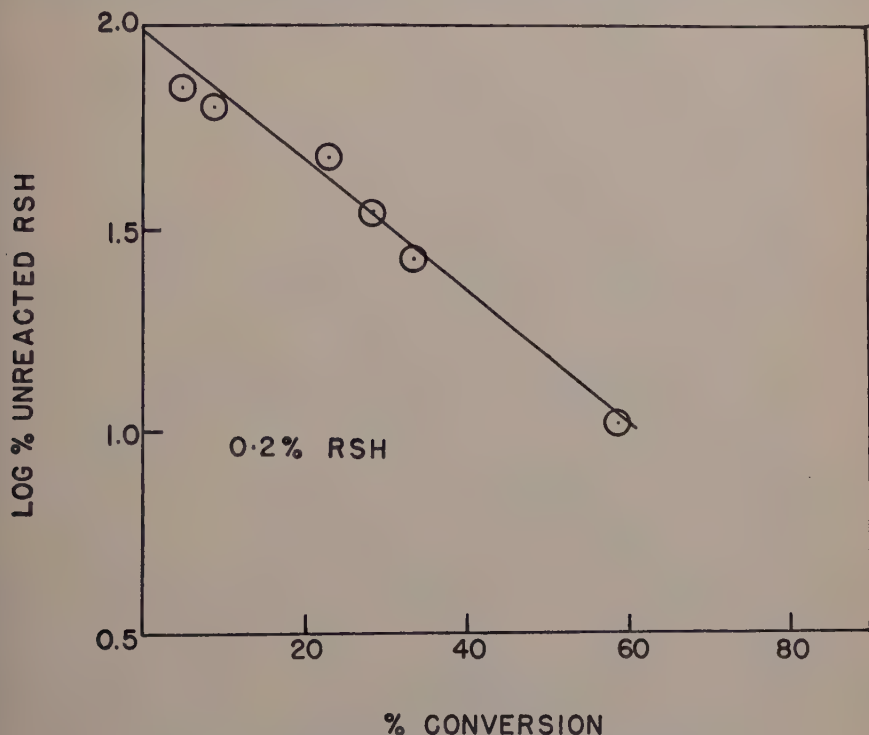


FIGURE 4. Rate of RSH disappearance in isoprene polymerization at 70°C.

since the benzene dilution technique leads to the true intrinsic viscosity of the polymer in benzene.

The viscosity-conversion curves obtained by this Vistex method are shown in FIGURES 5, 6, 7, and 8 for butadiene and isoprene polymerization in emulsion. The rising portion of the curves can be ascribed to the steadily increasing molecular weight of the polymer due to the kinetics of disappearance of the chain-transfer agent. At the gel-point, however, the higher molecular weight species begin to form networks of microgel which, although dispersed in the vistex solvent, do not contribute as much to the solution viscosity as they would if they were more linear and extended. Thus there is a peak in these curves which corresponds closely to the gel-point.

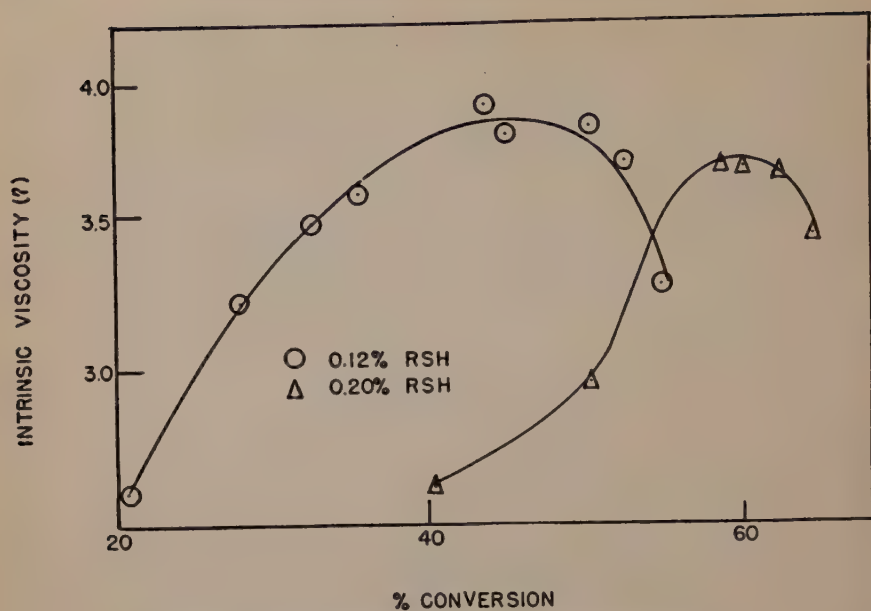


FIGURE 5. Intrinsic viscosity vs. conversion for polybutadiene at 40°C.

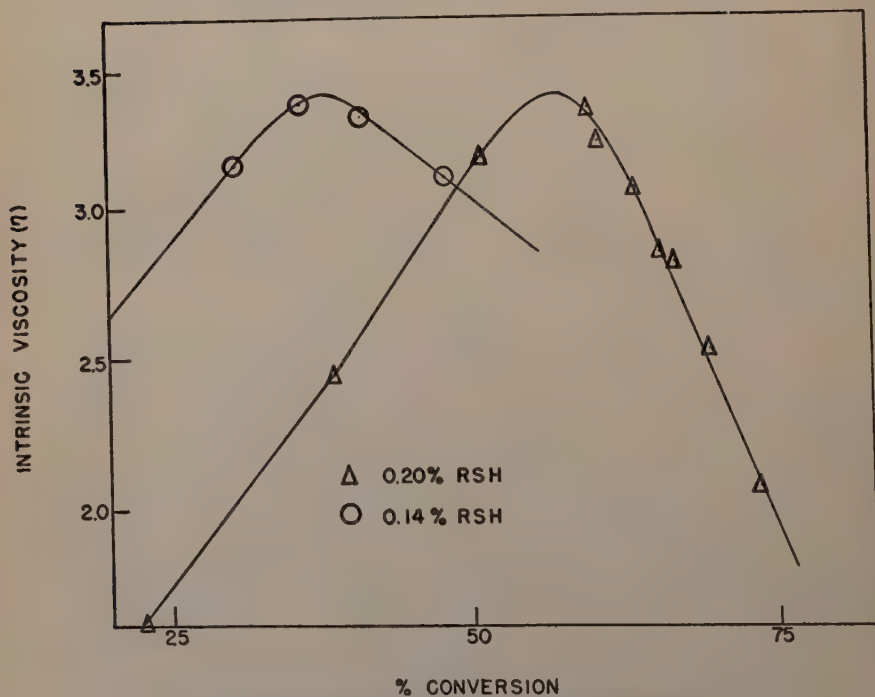


FIGURE 6. Intrinsic viscosity vs. conversion for polybutadiene at 50°C.

Crosslinking Rates for Butadiene and Isoprene

From the data on gel-points, monomer-polymer ratio, and primary chain lengths, the value of K , the relative crosslinking rate, can be calculated by means of EQUATIONS 5 and 7. The data used, and the results for such a calculation are shown in TABLE 1 for butadiene and isoprene at several temperatures. The value for the monomer-polymer ratio (m in EQUATION 5) used in this calculation was 0.85 for both butadiene and isoprene, a value which had been determined previously in this laboratory.

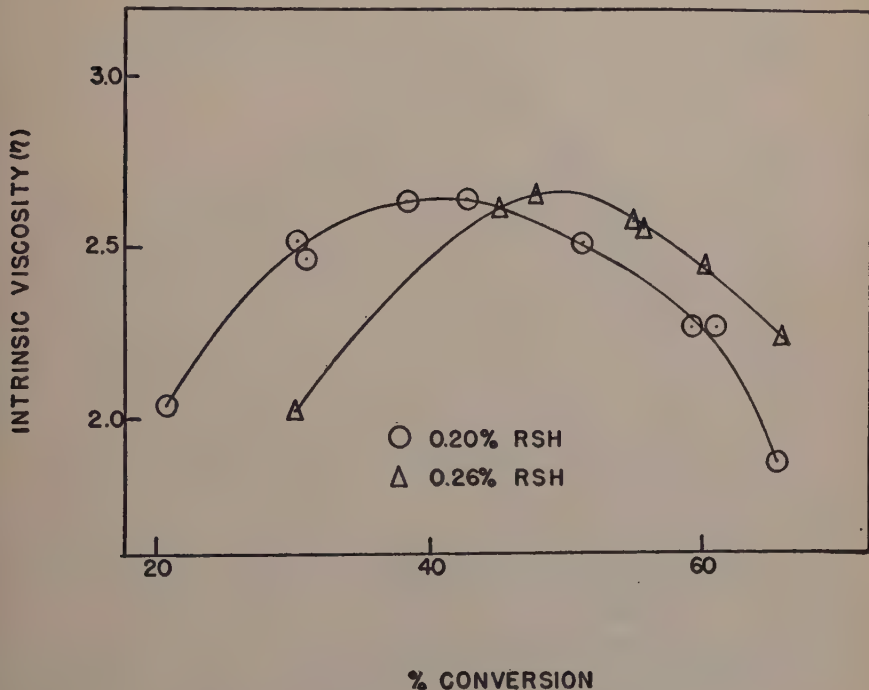


FIGURE 7. Intrinsic viscosity vs. conversion for polybutadiene at 60°C.

It can be seen that, at each temperature measured, reasonably good agreement was obtained for the calculated values of K , the relative crosslinking rate constant. The striking difference in crosslinking rate between the two monomers is obvious. The isoprene at 70°C. shows a crosslinking frequency only about one-fifth that of butadiene at 60°C., hence the polyisoprene chains can grow to a weight-average length of over 10^6 units before gelation, whereas the polybutadiene forms gel when the weight-average chain length (at 60°C.) becomes about 2×10^4 units. This is also illustrated by the much lower concentration of thiol used in the isoprene polymerization as compared to that of the butadiene. It should be emphasized that sufficient evidence is available that, for both monomers, chain transfer with the thiol is the principal mechanism for termination of growing chains.

The temperature coefficient of the relative crosslinking rate for butadiene enables a calculation of the difference in activation energy between the crosslinking reaction (E_x) and the propagation reaction (E_p). The value obtained

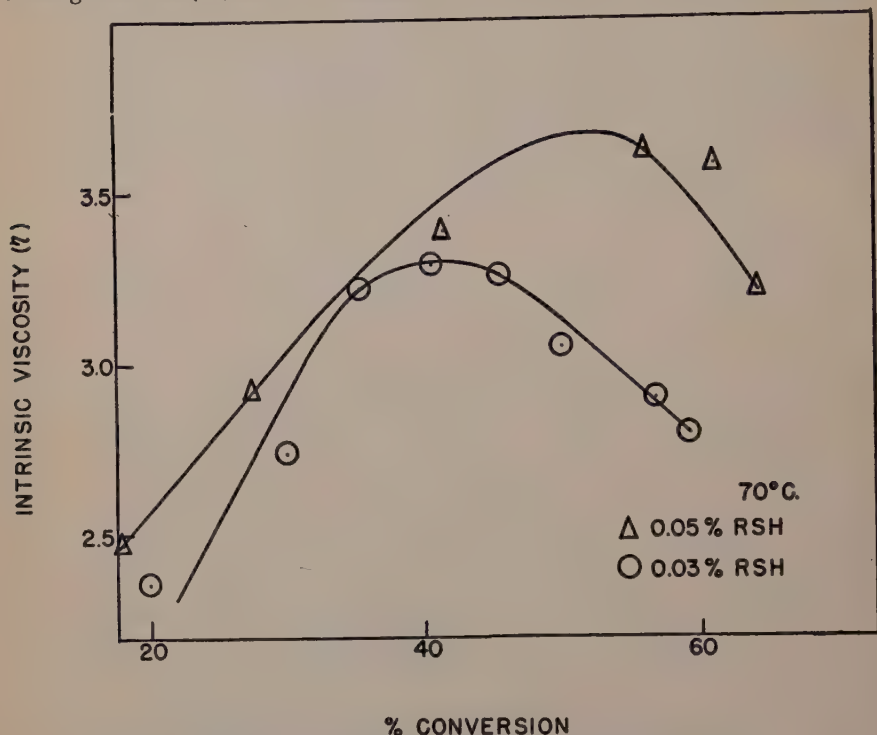


FIGURE 8. Intrinsic viscosity vs. conversion for polyisoprene at 70°C.

TABLE 1
RELATIVE CROSSLINKING RATE CONSTANTS

Temp. (°C.) T_g	Butadiene						Isoprene	
	40 4.32	50 3.83	60 3.26	70 3.33				
RSH Charge (R_0) (moles/mole monomer $\times 10^4$)	3.30	5.60	3.70	5.80	5.80	7.22	0.87	1.45
Gel-point conversion (α_g)	0.46	0.60	0.38	0.57	0.40	0.50	0.40	0.52
\bar{y}_w at gel-point ($\times 10^{-3}$)	4.43	3.93	3.03	3.22	2.17	2.13	13.1	11.2
ρ at gel-point ($\times 10^4$)	2.25	2.54	3.30	3.10	4.60	4.69	0.77	0.89
K ($\times 10^4$)	0.96	1.08	1.40	1.32	1.96	1.99	0.33	0.38

for $E_x - E_p$ from these data is 7.5 ± 0.5 kg. calories. This has the effect of approximately doubling the relative crosslinking rate for every 20°C. rise in temperature.

Branching by Chain Transfer

As stated previously, the crosslinking reaction is not affected to any extent by chain branching of the type illustrated in reactions (2) and (3), hence the data shown above do not offer any indication of the extent of such branching reactions. A consideration of the molecular weight relationships, however, can be used to show that the crosslinking reaction is predominant over the branching reaction under the conditions studied. It is obvious that, although the number-average molecular weight is not affected by such branching reactions, the weight-average (or viscosity-average) should be. From statistical considerations it is possible to calculate the "viscosity heterogeneity index" *i.e.*, \bar{y}_w/\bar{y}_n for polymer formed at any given instant. This has been found¹³ to be

$$\frac{\bar{y}_w}{\bar{y}_n} \simeq \left\{ \Gamma (2 + a) \right\}^{\frac{1}{a}}$$

where "*a*" is the empirical coefficient in the relation between intrinsic viscosity and degree of polymerization given by $[\eta] = K_v y_v^a$.

Measurements¹⁴ at very low conversions (*circa* 5 per cent) in GR-S polymerization have yielded a value of 1.84 for \bar{y}_w/\bar{y}_n , which agrees very well with the calculated value of 1.85 ($a = 0.67$ for this polymer in benzene¹⁵). This can be taken to indicate a negligible extent of branching by chain transfer with the polymer, especially so since the polymerization can be considered as occurring largely in the polymer-monomer particles (high concentration of polymer) even at this low conversion. Furthermore, at such low conversion, the crosslinking reaction does not form any substantial networks because of the relatively small primary chains. As the polymerization proceeds, however, the increasing chain length leads to increasing network formation by crosslinking, causing a marked effect on the molecular weight distribution. This is strikingly illustrated by the sharp rise in the value of \bar{y}_w/\bar{y}_n . Thus, at the gel-point of butadiene at 50°C., this value rises to about 4.5 instead of the theoretical value of about 2, based on thiol depletion kinetics and the value of $a = 0.45$ for polybutadiene polymerized in this system.¹⁶ Thus there seems to be a strong indication that "branching" in diene polymerization occurs largely through the crosslinking reaction.

References

1. FLORY, P. J. 1947. J. Am. Chem. Soc. **69**: 2893.
2. STOCKMAYER, W. H. 1944. J. Chem. Phys. **12**: 125.
3. MEYER, A. W. 1949. Ind. Eng. Chem. **41**: 1570.
4. HARKINS, W. D. 1947. J. Am. Chem. Soc. **69**: 1428.
5. SNYDER, H. R., J. M. STEWART, R. E. ALLEN, & R. J. DEARBORN. 1946. J. Am. Chem. Soc. **68**: 1422.
6. WALL, F. T., F. W. BANES, & G. D. SANDS. 1946. J. Am. Chem. Soc. **68**: 1429.
7. EWART, R. H., W. V. SMITH, & G. E. HULSE. Private Communication to Office of Rubber Reserve.
8. MORTON, M. & R. V. V. NICHOLLS. 1947. Can. J. Research. **B25**: 159.
9. MCLEAN, D. B., M. MORTON, & R. V. V. NICHOLLS. 1949. Ind. Eng. Chem. **41**: 1622.
10. BARDWELL, J. & C. A. WINKLER. 1949. Can. J. Research **B27**: 116, 128, 139.

11. BAKER, W. O. 1949. Ind. Eng. Chem. **41**: 511.
12. HENDERSON, D. A. & N. R. LEGGE. 1949. Can. J. Research **B27**: 666.
13. REHNER, J. 1944. Ind. Eng. Chem. **36**: 118.
14. HARRIS, W. E. & I. M. KOLTHOFF. 1947. J. Polymer Sci. **2**: 72.
15. FRENCH, D. M. & R. H. EWART. 1947. Ind. Eng. Chem., Anal. Ed. **19**: 165.
16. JOHNSON, B. L. & R. D. WOLFANGEL. 1949. Ind. Eng. Chem. **41**: 1580.

BRANCHING BY LONG CHAIN SUBSTITUENTS

By H. Mark

Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

Introduction

This paper presents a brief review of a kind of branching which is quite different from that discussed in the other papers of this symposium, namely branching which is caused by the attachment of long chain fatty alcohols or acids to the macromolecules of polymeric acids or alcohols. The length of the "branches" varied from one to 18 carbon atoms; the polymer molecules were polyacrylic acid, polymethacrylic acid, polyvinylacetate, and cellulose. In contrast to the random branching reported in the other contributions of this volume the long chain substituents are attached to the backbone chain of the base polymer in regular distances and in regular configuration, they have all the same length and shape. This type of branching has therefore been called "feather branching." The uniform spacing, uniform length, and uniform structure of the individual branches makes it possible for them to undergo a crystallization phenomenon on their own which is superimposed on whatever crystallization or lateral order can be exhibited by the backbone chains. Here it is advantageous to distinguish two cases, namely:

(1) The backbone polymer is capable to crystallize on its own, such as cellulose and polyvinylalcohol.

(2) The backbone polymer is intrinsically amorphous such as polyacrylic acid and polymethacrylic acid.

In the first case, compounds with short side chains, such as cellulose acetate, propionate, and butyrate follow the pattern of lateral order exhibited by the base polymer. The branches act as substituents which modify but do not destroy the characteristic features of the cellulose lattice. The compounds possess a first order transition point* (melting point), like all crystalline polymers which, however, is lower than that of the base polymer. Apparently, the substituents, which are relatively non-polar, increase the distances between the polymer chains and hereby reduce their mutual molecular attraction. They act like "ingrown" or "chemical" plasticizers.

As the length of the branches increases, this plasticizing effect becomes so strong that the polymer chains are no longer capable of maintaining a stable lattice structure and the melting point decreases rapidly. If the number of carbon atoms of the esterifying acids is between 6 and 10, a minimum in the softening temperature is reached and the x-ray diagram presents essentially the pattern of an amorphous material. The crystallization tendency of the backbone chains is greatly reduced and that of the branches is not yet large enough to manifest itself. The softening points in this range are, therefore, probably not clean first order melting points, but transition phenomena of a more complicated nature.

* Because of the presence of a certain amount of laterally disordered or amorphous material, all samples also show one or more second order transition points which are much lower than the melting temperature of the crystalline domains.

If, now, the length of the branches is further increased, their own tendency for lateral order becomes appreciable, and they form a crystal lattice of their own character. As a consequence, the softening point of these compounds rises again and the x-ray diagrams reveal the characteristics of a long chain fatty acid lattice. In the range of short chain substituents, one is faced with a plasticized cellulose type lattice. In the domain of long chain substituents, one has very small crystalline areas with a paraffin lattice which are linked together and threaded up by the connecting cellulose chains. In the case of polyvinyl-alcohol, the first part of this characteristic behavior cannot be clearly established because the backbone chains of this material are much less regular than those of cellulose and, already, short chain substituents, such as acetate and propionate, plasticize the backbone polymer so much, that an essentially amorphous structure results. Because of the higher flexibility of the polyvinylalcohol backbone chain as compared with cellulose, however, relatively short side chains such as C_{12} and C_{14} already show distinct side chain crystallization and the formation of a fatty acid type lattice with first order melting points.

If the backbone chains cannot crystallize, such as in the case of polyacrylates and polymethacrylates, only second order transition phenomena are encountered until the length of the branches becomes so appreciable that they manage to establish lateral order on their own. The x-ray diagrams now indicate the presence of a fatty acid type lattice and the transition phenomena of these materials probably consist of first order melting of the crystalline domains superimposed to second order softening of the amorphous constituents.

The cooperation of backbone and side chain crystallization leads to very interesting thermal behavior and solubility characteristics of these compounds. Only a limited number have been prepared and studied up to date. Some were only of relatively low molecular weight and might not have exhibited the full characteristics of a polymer.

The following TABLES 1 to 5 are added to convey a more precise and quantitative notion of the general remarks made in this introduction.

Polyvinylesters

In a series of excellent papers, Swern and his collaborators¹ have prepared a large number of esters of unsaturated alcohols with fatty acids ranging from acetic acid to stearic acid. They have polymerized all these compounds and have specifically studied the thermal properties of fatty acid vinyl esters which had molecular weights in the range from 100,000 to 700,000. At room temperature, the polyvinylesters of caprylic, capric, and lauric acid are viscous liquids. Those of myristic, palmitic, and stearic acid are waxy solids. They exhibit sharp, first order transition phenomena which can be established with the refractometric method and with the polarizing microscope. A few figures are given in TABLE 1. They show that the melting points of these materials increase with the chain length of the branch, although no influence of the chain length of the connecting backbone chain was noticeable. In comparing the values of the transition points of the polyvinylesters with the melting points of the corresponding ethylesters (which are also shown in the table), it can be

seen that the former are always somewhat higher than the latter. This difference apparently expresses the reinforcing action of the polyvinyl chain which links the fatty acid residues together and reduces the entropy gain that accompanies the fusion of the side chain crystals. In a more recent paper, copolymers of vinylacetate with vinylpalmitate, vinylstearate and vinyloleate were investigated.² Acetate and oleate did not show any first order transition phenomena over the whole composition range, but only typical brittle points. This is not surprising in view of the well known reluctance of oleic acid to crystallize. Copolymers of the acetate and stearate exhibit sharp melting points down to a stearate content of about 43 per cent by weight, whereas copolymers of acetate and palmitate gave melting points only down to a palmitate content of about 73 per cent. Both series of copolymers showed typical brittle

TABLE 1

FIRST ORDER TRANSITION POINTS OF A FEW POLYVINYL FATTY ACID ESTERS IN °C.

Substance	Transition point	Substance	Transition point
Polyvinyl-laurate	1.0	Ethyl-laurate	-1.68
Polyvinyl-myristate	15.5	Ethyl-myristate	10.2
Polyvinyl-palmitate	34.5	Ethyl-palmitate	24.2
Polyvinyl-stearate	45.6	Ethyl-stearate	33.7

TABLE 2

FIRST ORDER TRANSITION POINTS OF A FEW COPOLYMERS VINYLACETATE WITH VINYL-PALMITATE AND VINYLSTEARATE IN °C.

System Acetate-palmitate	Transition point	System Acetate-stearate	Transition point
100 % palmitate	~40°	100 % stearate	~51°
89.3% palmitate	31°	91.8% stearate	45°
73.1% palmitate	25°	76.7% stearate	40°
		61.6% stearate	38°
		53.3% stearate	34°
		42.8% stearate	32°

points at higher acetate contents. TABLE 2 contains a few figures, they show clearly that the melting points of the copolymers steadily decrease with increasing acetate content, as one would expect, because of the diluting and disturbing effect of these small substituents on the crystallization of the longer fatty acid chains. At a certain critical acetate concentration along the length of the polymer chain, side chain crystallization is no longer possible and one obtains amorphous materials which exhibit only second order transition phenomena. The superior crystallization tendency of stearic acid (18 carbon atoms) as compared with palmitic acid (16 carbon atoms) is very clearly demonstrated by these interesting experiments.

Polyalkylacrylates, and Methacrylates

Rehberg and Fisher³ synthesized the series of alkylacrylates from methyl to hexadecyl, prepared their polymers, and described the basic properties of the

monomers and polymers. Specifically, they determined the brittle points of several polyacrylates from methyl to hexadecyl, which are given in TABLE 3 and exhibit the characteristic behavior mentioned in the first paragraph of this article. Polymethylacrylate has a brittle point around 2°C; the introduction of alkylresidues of increasing length spaces the backbone chains farther apart, facilitates the movement of their segments, produces plasticization, and leads to lower and lower brittle points until a minimum of -63°C is reached at the octylester. Later, the brittle points increase again and reach values around 40°C for the hexadecylester. According to the x-ray studies of Kaufman, Sacher, Alfrey and Fankuchen⁴ the esters of the higher aliphatic alcohols show

TABLE 3
BRITTLE POINTS AND SECOND ORDER TRANSITION POINTS OF SEVERAL
POLY ALKYLACRYLATES

Material	Brittle point in °C.	Transition point °C.
Polymethylacrylate	2	0
Polyethylacrylate	-25	-25
Polybutylacrylate	-43	—
Polyhexylacrylate	-58	—
Polyoctylacrylate	-63	—
Polydodecylacrylate	0	—
Polytetradecylacrylate	20	20
Polyhexadecylacrylate	38	35

TABLE 4
TRANSITION POINTS OF A FEW POLYALKYLMETHACRYLATES

Material	Transition point in °C.	Material	Transition point in °C.
Polymethyl-methacrylate	72	Polyoctyl-methacrylate	-55
Polyethyl-methacrylate	47	Polydecyl-methacrylate	-55
Polypropyl-methacrylate	33	Polytetradecyl-methacrylate	-9
Polybutyl-methacrylate	17		

the characteristic pattern of a fatty acid lattice which indicates side chain crystallization and would make it probable that these substances exhibit first order transition phenomena.

Transition points of this series have been determined with the refractometric and microscopic method by Wiley and Brauer;⁵ they are included in TABLE 3 and correspond closely to the brittle points observed by Rehberg and Fisher.

It may be interesting to note that the C₁₄ and C₁₆ polyalkylacrylates have very nearly the same melting points as the C₁₄ and C₁₆ polyvinyl fatty acid esters. Apparently they represent about the same compromise between the crystallization tendency of the branches and the reinforcing action of the backbone chains. Corresponding experiments with alkylesters of polymethylacrylic acid gave the figures contained in TABLE 4. They show that the somewhat stiffer macromolecules of the methacrylic acid with a transition point of 72°C for the methylester, are more difficult to plasticize than the softer polyacrylic acid chains. The butylester of polymethacrylic acid has a transition point of 17°C

against -70°C for polybutylacrylate. This greater stiffness of the back bone chain also seems to delay side chain crystallization as shown by the low second order transition point of -9°C for the tetradecylester. No higher esters of polymethacrylic acid have as yet been investigated, but it would be very interesting to see whether eventually side chain crystallization can be obtained if the branches are sufficiently long. Equally interesting would be a study of copolymers of docecyl, tetradecyl and hexadecyl acrylates and methacrylates where side chain crystallization should be expected to occur.

Fatty Acid Esters of Cellulose

Hagedorn and Moeller⁶ had already prepared and studied in 1931 the higher fatty acid triesters of cellulose and found that they exhibited waxy properties and showed an x-ray diagram with the pattern of a paraffin. Their findings were confirmed and extended by Malm, Mench, Kendall and Hiatt⁷ in an extensive study of the preparation and properties of these materials from the triacetate to the tripalmitate. The synthesis was carried out by reaction of the acrylchlorides on cellulose in the presence of pyridin, which prevented, or

TABLE 5
MELTING AND SOFTENING POINTS OF SEVERAL TRIESTERS OF CELLULOSE

Material	Transition point in $^{\circ}\text{C}$.	Material	Transition point in $^{\circ}\text{C}$.
Triacetate	300	Caprate	88
Tributyrate	183	Laurate	91
Tricaproate	94	Palmitate	105
Triheptylate	88	Stearate	—
Tricaprylate	86		

at least, minimized the degradation of the cellulose during acrylation. Many properties of the various triesters were studied, amongst them the melting points which are given in TABLE 5. The first two members—cellulose triacetate and cellulose tributyrat—exhibit sharp x-ray diagrams which are characteristic for the cellulose type lattice. The melting points of the crystalline domains are high and show typical first order transition point behavior.⁸ The following triesters give x-ray diagrams of decreasing sharpness and distinction, their softening points are all very similar (94, 88, 86, and 91) and are probably second order transitions. From the palmitate on the x-ray, patterns are of the fatty acid type and indicate side chain crystallization, the softening points rise again and appear to be normal melting points of the crystalline domains formed by lateral order of the branches. In this case, the rather stiff chains of the cellulose backbone polymer increase the melting point of the side chain crystallites considerably above the normal melting point of the corresponding fatty acid (about 100°C against about 50°C) and produce a substantial hardening and toughening of the system.

References

1. SWERN, D., W. S. PORT, J. E. HANSEN, E. F. JORDAN, J. W. O'BRIEN, & T. J. DIETZ. 1947. *J. Am. Chem. Soc.* **69**: 2439; 1948. *Ibid.* **70**: 2334; 1949. *Ibid.* **71**: 2377;

1952. *Ibid.* **74**: 1738; 1951. *J. Polymer Sci.* **7**: 207; 1952. *Ibid.* **9**: 493; 1951. *Ind. Eng. Chem.* **34**: 2105.
2. PORT, W. S., E. F. JORDAN, JR., J. E. HANSEN, & D. SWERN. 1952. *J. Polymer Sci.* **9**: 493.
 3. REHBERG, C. E. & C. H. FISHER. 1944. *J. Am. Chem. Soc.* **66**: 1203.
 4. KAUFMAN, H. S., A. SACHER, T. ALFREY, & I. FANKUCHEN. 1948. *J. Am. Chem. Soc.* **70**: 3147.
 5. WILEY, R. H. & G. M. BRAUER. 1948. *J. Polymer Sci.* **3**: 647.
 6. HAGEDORN, M. & P. MOELLER. 1931. *Cell. Chem.* **12**: 29.
 7. MALM, C. J., J. W. MENCH, D. L. KENDALL, & G. D. HIATT. 1951. *Ind. Eng. Chem.* **43**: 684, 688.
 8. FLORY, P. J. & L. MANDELKERN. 1951. *J. Am. Chem. Soc.* **73**: 3206.

MONOGRAPHIC PUBLICATIONS
OF
THE NEW YORK ACADEMY OF SCIENCES
(LYCEUM OF NATURAL HISTORY, 1817-1876)

(1) The ANNALS (octavo series), established in 1823, contain the scientific contributions and reports of researches, together with the records of meetings of the Academy. The articles which comprise each volume are printed separately, each in its own cover, and are distributed immediately upon publication. The price of the separate articles depends upon their length and the number of illustrations, and may be ascertained upon application to the Executive Director of the Academy.

Current numbers of the ANNALS are sent free to all Members of the Academy desiring them.

(2) The SPECIAL PUBLICATIONS established in 1939, are issued at irregular intervals as cloth-bound volumes. The price of each volume will be advertised at time of issue.

(3) The MEMOIRS (quarto series), established in 1895, are issued at irregular intervals. It is intended that each volume shall be devoted to monographs relating to some particular department of Science. Volume I, Part 1, is devoted to Astronomical Memoirs, Volume II to Zoological Memoirs. No more parts of the Memoirs have been published to date. The price is one dollar per part.

(4) The SCIENTIFIC SURVEY OF PORTO RICO AND THE VIRGIN ISLANDS (octavo series), established in 1919, gives the detailed reports of the anthropological, botanical, geological, paleontological, zoological, and meteorological surveys of these islands.

Subscriptions and inquiries concerning current and back numbers of any of the publications of the Academy should be addressed to

EXECUTIVE DIRECTOR
The New York Academy of Sciences
2 East Sixty-third Street
New York 21, N. Y.

